TITLE OF THE INVENTION

ELEMENT HAVING PORPHYRIN POLYMER FIXED ON A SUBSTRATE
AND METHOD OF PREPARING THE SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is based upon and claims the
benefit of priority from prior Japanese Patent
Application No. 2003-054719, filed February 28, 2003,
the entire contents of which are incorporated herein by
reference.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to an element
having, on a substrate, a porphyrin polymer fixed by
covalent bonds, and a method of producing the same.
The element can be used as a photo-functional molecule
material, and more specifically, as a photoelectric
conversion element such as an organic solar cell or
a three-dimensional, non-linear organic material.

2. Description of the Related Art

It is expected that a porphyrin polymer can
be used as a media having high performance light-
collecting medium and electron transport such as
observed in chloroplast of green plants and photo-
synthetic bacteria. It is assumed that a porphyrin
polymer can be applied to a molecule element such as
an organic solar cell and photo-semiconductor and by
providing porphyrin on an electrode by way of chemical

modification. As a method of producing a porphyrin polymer thin film in which arrangement of porphyrin unit is controlled at the molecular level, the alternately-laminating method has been reported. Kunitake et al. has produced a porphyrin multi-layer film by alternately laminating polycationic and polyanionic porphyrins (K. Ariga, Y. Lvov and T. Kunitake, J. Am. Chem. Soc. 1997, 119, 2224-2231). Alternatively, porphyrins can be fixed on a substrate by alternately laminating a metal ion and porphyrin having metal ligand (D.J. Quian, C. Nakamura, T. Ishida, S.O. Wenk, T. Wakayama, S. Takeda and J. Miyake, Langmuir 2002, 18, 10237-10242). Photoelectric conversion has also been attempted by constructing a gradient of potential in such a porphyrin multi-layer film as described above (K. Araki, M.J. Wagner and M.S. Wrighton, Langmuir, 1996, 12, 5393-5398; F.B. Abdelrazzaq, R.C. Kwong and M. E. Thompson, J. Am. Chem. Soc. 2001, 124, 4796-4803; and A. Ikeda, T. Hatano, S. Shinkai, T. Akiyama and S. Yamada, J. Am. Chem. Soc. 2001, 123, 4855-4856).
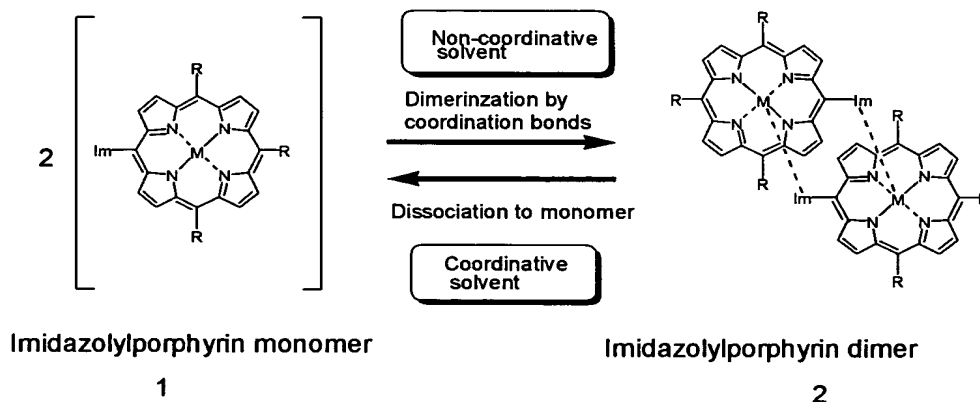
Further, it is known that porphyrin functions as a p-type semiconductor. There has been a report in which a p-n/p-p' junction interface was produced by a porphyrin film laminated by CVD or with electrolytically-polymerized films, and production of a photoelectric conversion element, a photo-rectification

interface or a Schottky diode was attempted (F.J.
Kampas and M. Gouterman, J. Phys. Chem. 1977, 81,
690-695; F. J. Kampas, K. Yamashita and J. Fajer,
Nature 1980, 284, 40-42; and Y. Harima and K.
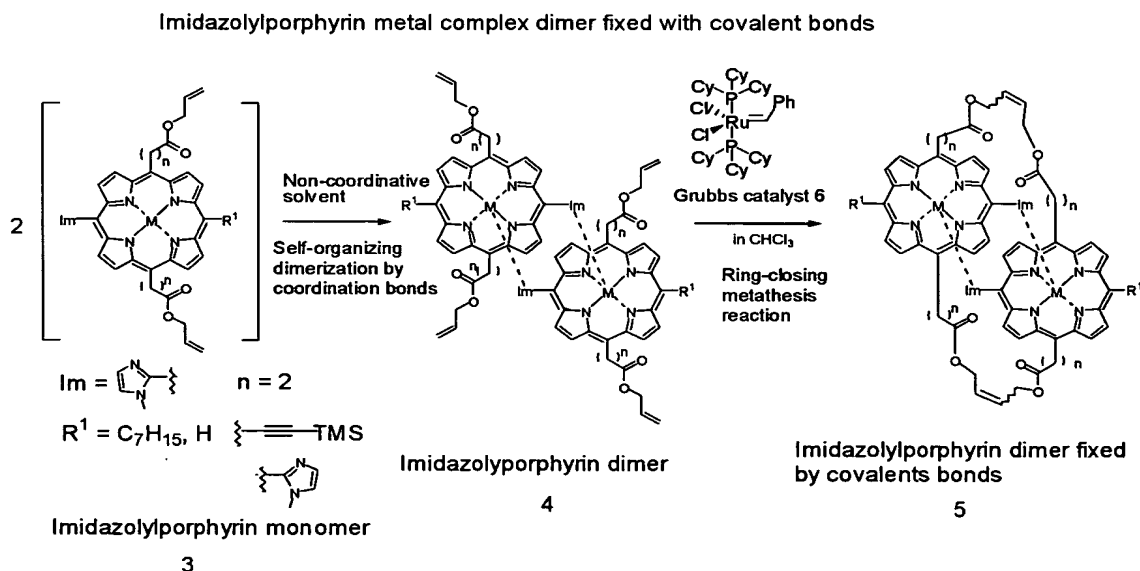Yamashita, J. Phys. Chem. 1985, 89, 5325-5327).

On the other hand, the inventors of the present
invention have discovered that imidazole-substituted
porphyrin metal complexes coordination-bond in
a complementary manner between molecules, thereby
forming a hyper molecular structure similar to a dimer
observed in photosynthetic bacteria, as shown below
(Y. Kobuke and H. Miyaji, J. Am. Chem. Soc., 1994, 116,
4111-4112):

Dimerization of imidazolylporphyrin by coordination bonds and its dissociation

Non-coordinative solvent

Dimerinzation by coordination bonds

Dissociation to monomer

Coordinative solvent

Imidazolylporphyrin monomer
1

Imidazolylporphyrin dimer
2

The characteristics of the above-described
porphyrin dimer reside in that the porphyrin dimer is
capable of absorbing light in a significantly wide
wavelength range owing to exciton division and that
the charge-dissociated state can be prolonged because
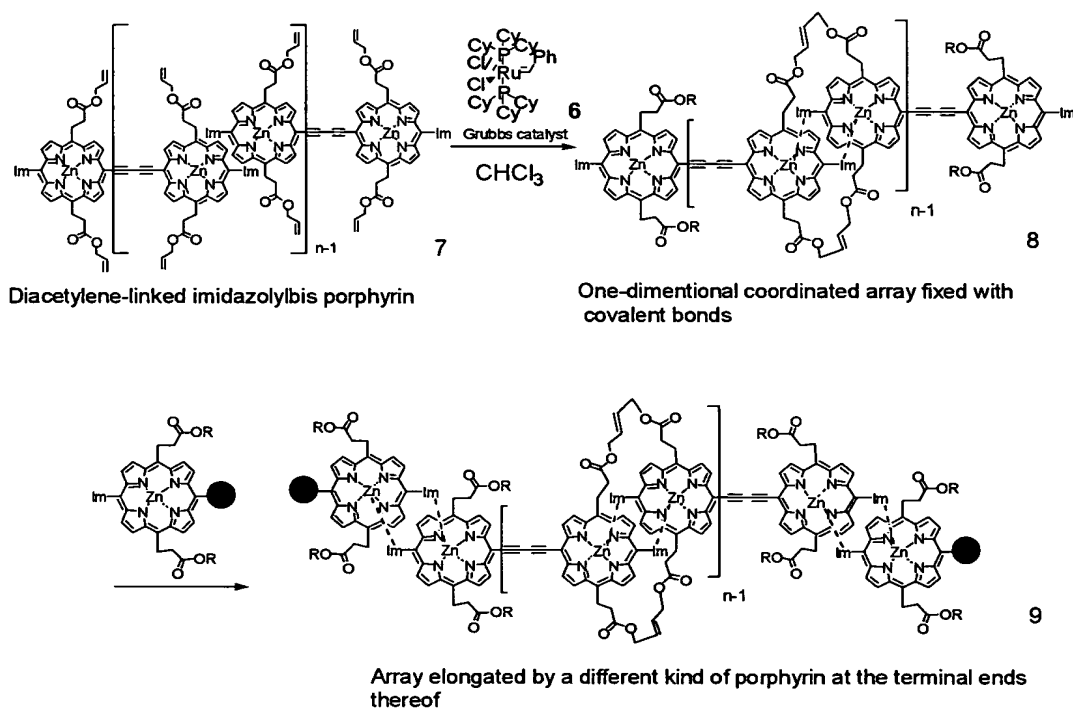the exciton species is present between the dimer in

a non-localized manner. Accordingly, the porphyrin

dimer enables a very efficient photosensitization

reaction. Further, when a side-chain allyl substituent

is introduced to the imidazole-substituted porphyrin,

5   the dimer structure can be fixed by covalent bonds

through a metathesis ring-closing reaction using

a Grubbs complex. The electronic spectrum of the dimer

structure fixed by covalent bonds was not affected by

a solvent and exhibited a strong exciton interaction

10   (The gist of lecture 2-2 at 82th Organic Synthesis

Symposium, p.65-68 (2002).

Imidazolylporphyrin metal complex dimer fixed with covalent bonds

Im = [structure]   n = 2

$R^1 = C_7H_{15}$, H   [structure]—≡—TMS

Imidazolylporphyrin monomer
3

Imidazolyporphyrin dimer
4

Imidazolylporphyrin dimer fixed by covalents bonds
5

15   By using the above bis(imidazole-substituted

porphyrinatozinc) units fixed by covalent bonds, it is

now possible to design a hyper molecule structure which

has been made more highly multi-layered. Specifically,

the imidazole-substituted bis-porphyrin forms a one-

20   dimensionally extended, coordinated structural array

(K. Ogawa and Y. Kobuke, Angew. Chem. Int. Ed. 2000, 39, 4070-4073). By fixing the coordinated structural array with covalent bonds through a metathesis reaction in a step-by-step manner, next imidazole-substituted porphyrinatozinc having the functional groups can be introduced to the coordinate structural array and fixed thereto, in the step-by-step manner as shown below:
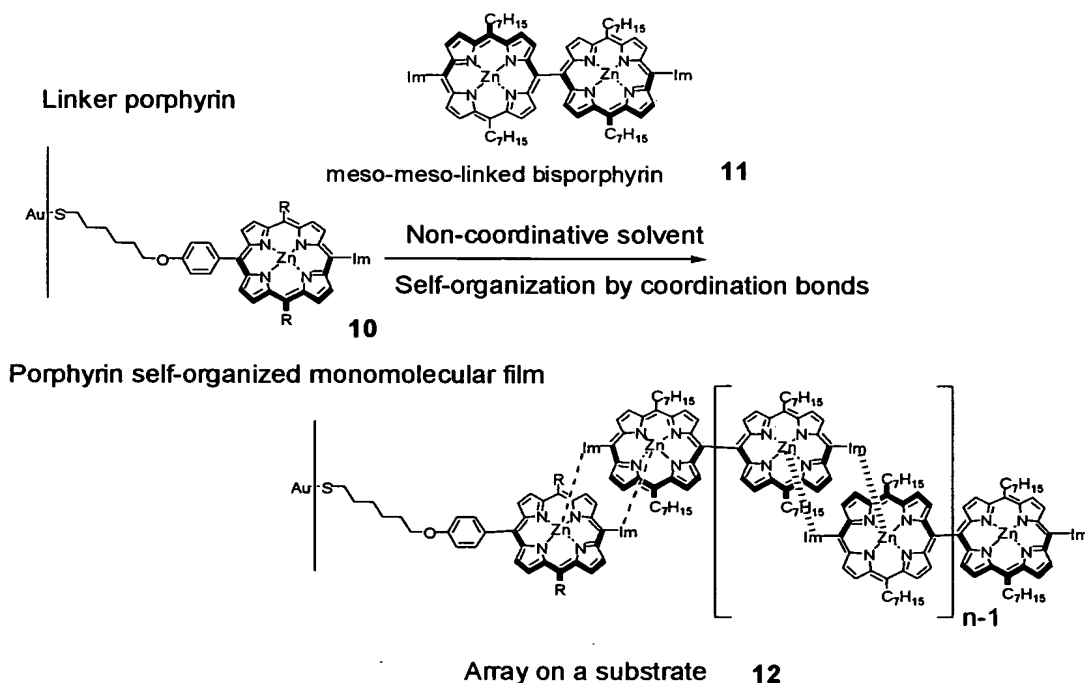
Fixation by covalent bonds of porphyrin polymer self-organized with coordination bonds

Diacetylene-linked imidazolylbis porphyrin

One-dimentional coordinated array fixed with covalent bonds

Array elongated by a different kind of porphyrin at the terminal ends thereof

In order to develop a practical device from such porphyrin polymer as described above, it is necessary to provide the porphyrin polymer on a solid substrate such as an electrode. In the study at the early stage, the inventors of the present invention conducted an experiment in which linker porphyrin was attached to a gold substrate and the substrate was soaked in a

solution of the imidazole-substituted porphyrinatozinc,
so that the porphyrin polymer was laminated on the
substrate by coordinate bond. The resulting element
which actually had a laminate structure was subjected
to photocurrent measurement and it was confirmed that
the element functioned properly as a photo-functional
element (A. Nomoto and Y. Kobuke, Chem. Commun.,
2002, 1104-1105).

Elongation, on a substrate, of imidazolylporphyrin polymer by coordination bonds

Linker porphyrin

meso-meso-linked bisporphyrin **11**

Non-coordinative solvent

Self-organization by coordination bonds

10

Porphyrin self-organized monomolecular film

Array on a substrate **12**

In order to improve the function of the above-
described element, it is necessary to provide, on
a solid substrate, porphyrin polymers of different
characteristics sequentially in a predetermined
direction. By providing porphyrin polymers in such a
manner, an element which loses less energy and enables

more efficient operation than the conventional element

can be constructed. In the aforementioned method in

which a substrate is simply soaked in a porphyrin

solution and allowed to form a laminate, the layer

5   which has been laminated on the substrate in the first

lamination step is peeled off when another layer is

laminated thereon in the second lamination step.

That is, in the aforementioned method, the first layer

is simply replaced with the second layer and it is

10   impossible to provide, on a solid substrate, porphyrin

polymers of different characteristics sequentially in

a predetermined direction.

BRIEF SUMMARY OF THE INVENTION

An object of the present invention is to solve the

15   above-described problems of the prior art and provide

a photo-functional molecule element which loses less

energy and effects more efficient operation than the

conventional element, and a method of producing the

same.

20   As a result of the keen study, the inventors of

the present invention have discovered that the above-

described problems can be solved by the following

photo-functional molecule element in which a photo-

functional molecule element composed of a covalently-

25   fixed porphyrin polymer is laminated on a substrate,

and the method of preparing the photo-functional

molecule element. Specifically, the present invention

provides a photo-functional molecule element laminated on a substrate represented by the following formula (VIII) or (VIII'):
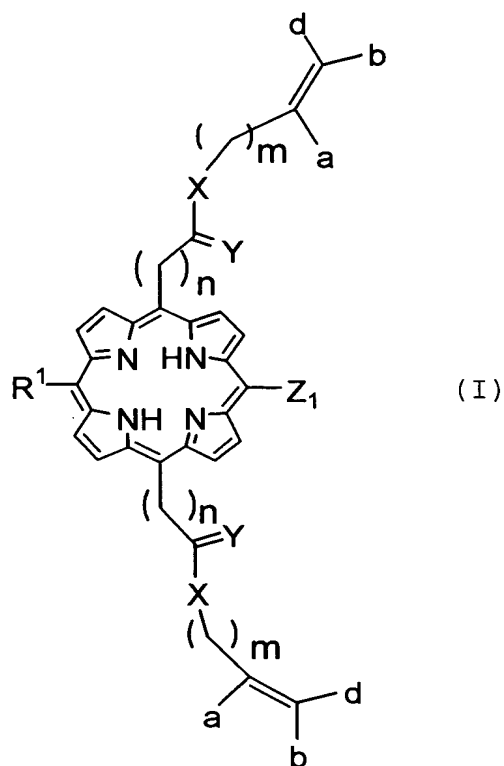
(VIII)

Substrate

(VIII')
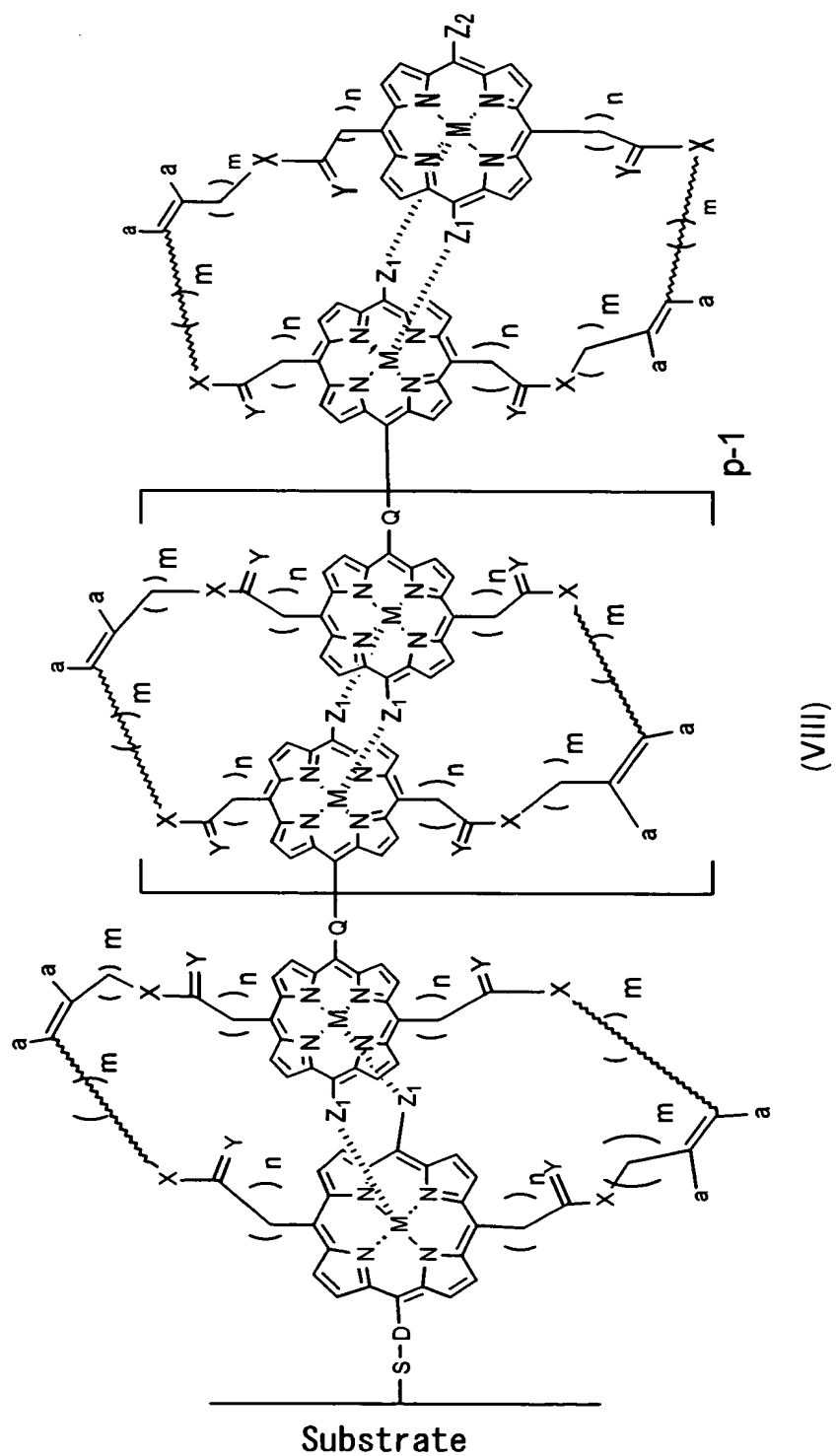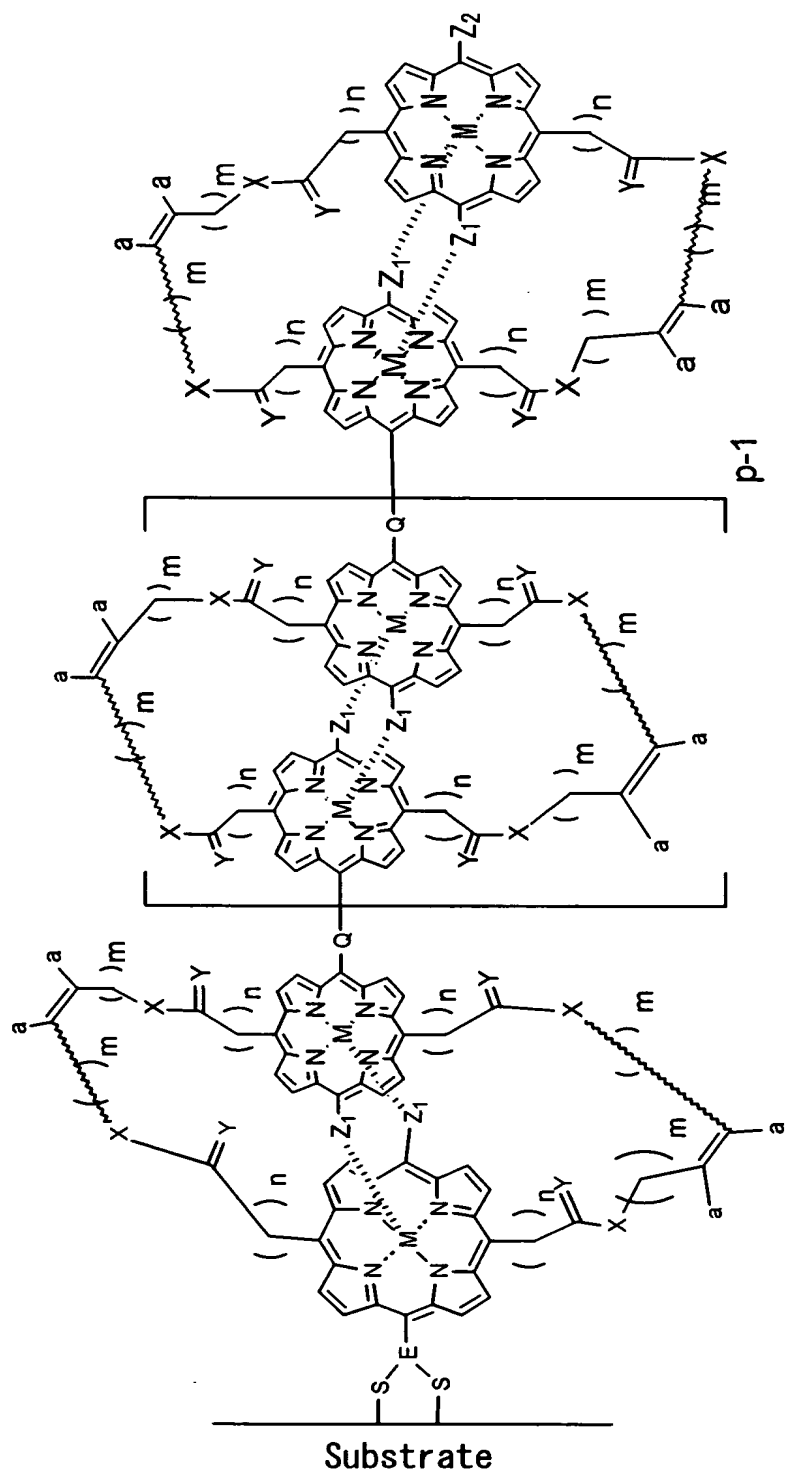
[wherein a represents H, alkyl group or aryl group; X represents $-O-$, $-S-$, $> NR_{101}$ (wherein R_{101} represents H or an alkyl group), CH_2 or single bond; Y represents $=O$, $=S$ or $2H$; m represents an integer of 0 to 4; n represents an integer of 0 to 6; Z_1 represents a 5- or 6-membered nitrogen-containing heteroaromatic ring group capable of forming a coordination bond; Z_2 represents a group having a functional group which can be an electron acceptor or electron donor, or a group which can be the terminal group of the porphyrin polymer; D represents a divalent group including at least one of arylene group and alkylene group; E represents a trivalent group including at least one of arylene group and alkylene group; M represents an ion of metal selected from the group consisting of typical metals and transition metals; Q represents a single bond or divalent linking group; and p represents an integer of 1 or more].

The present invention also provides the following method of producing the photo-functional molecule element in which a covalently-fixed porphyrin polymer has been laminated on a substrate. The method comprises:
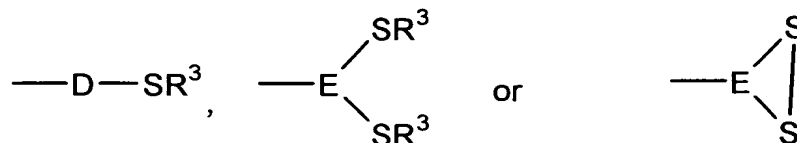
(1) fixing, on a substrate, a linker molecule represented by the following formula (I):

(I)

[wherein a, b and d independently represent H, an alkyl
group or aryl group; X represents $-O-$, $-S-$, $> NR_{101}$

5 (wherein R_{101} represents H or an alkyl group), CH_2 or
single bond; Y represents $=O$, $=S$ or $2H$; m represents an
integer of 0 to 4; n represents an integer of 0 to 6;
Z_1 represents a 5- or 6-membered nitrogen-containing
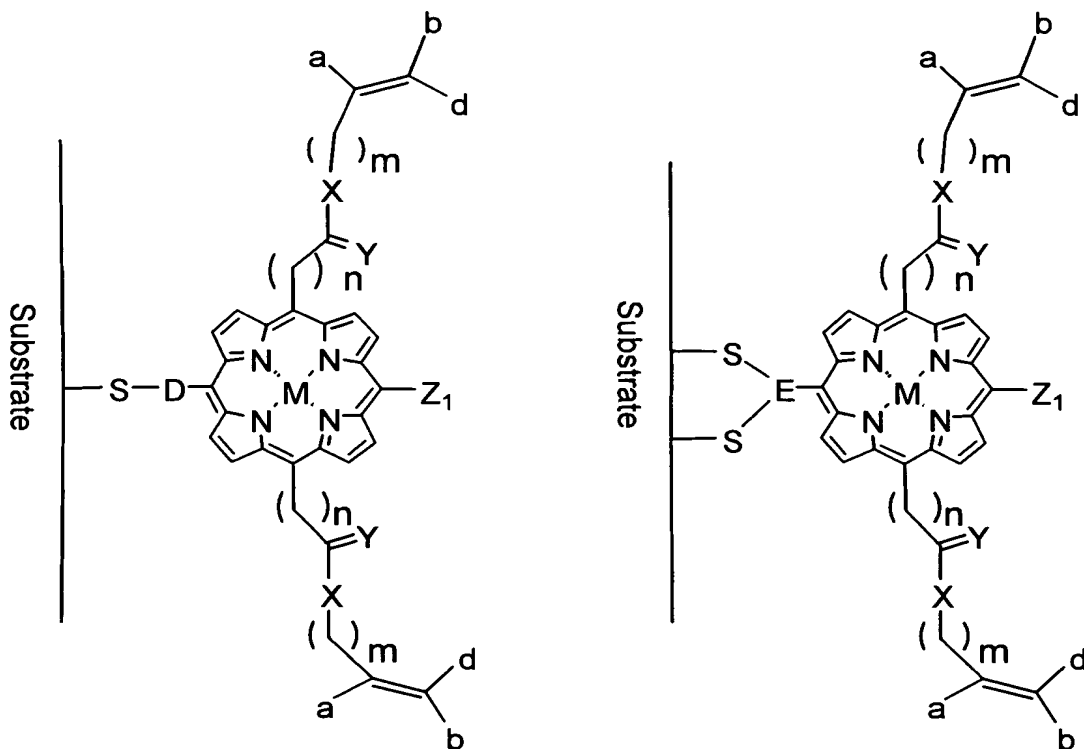heteroaromatic ring group capable of forming a

10 coordination bond; and R^1 represents

(wherein D represents a divalent group including at
least one of arylene group and alkylene group;

15 E represents a trivalent group including at least one

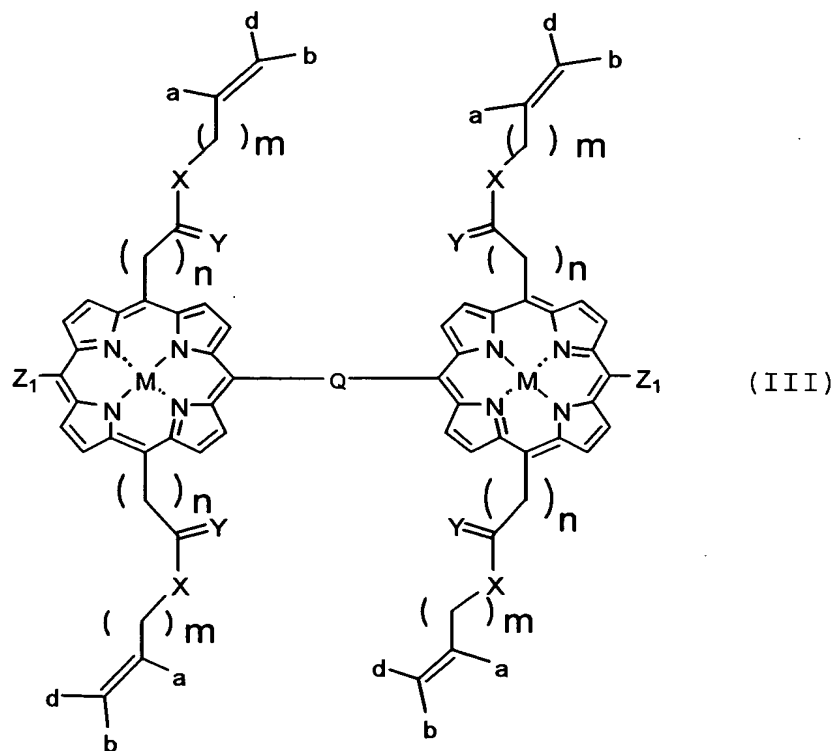of arylene group and alkylene group; and R^3 represents H or an acetyl group)]; and

introducing a metal M selected from the group consisting of typical metals and transition metals to the porphyrin residue derived from the linker molecule,

thereby obtaining a monomolecular film represented by the following formula (II) or (II'):
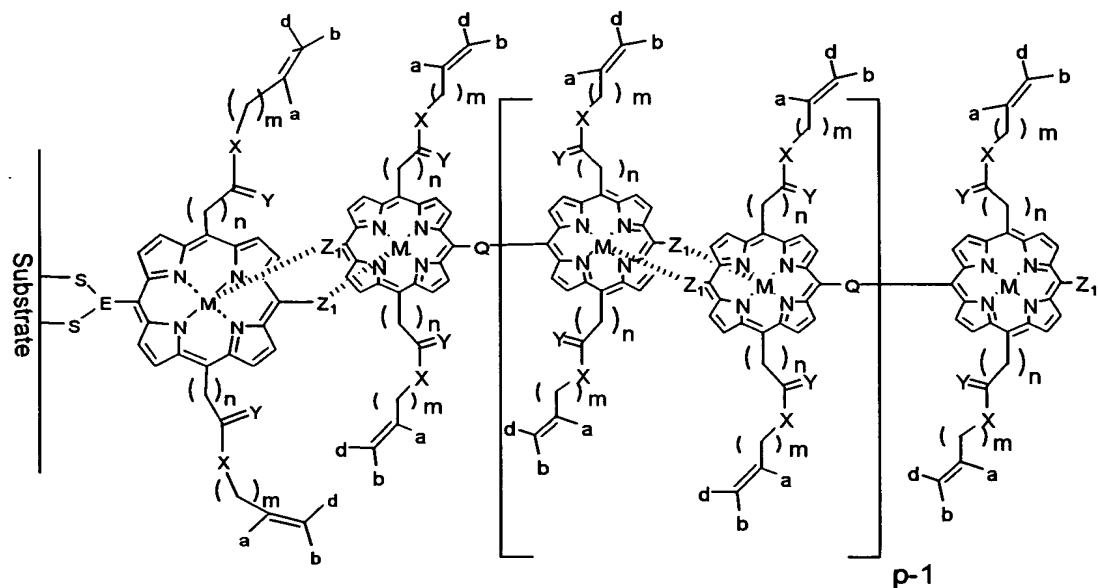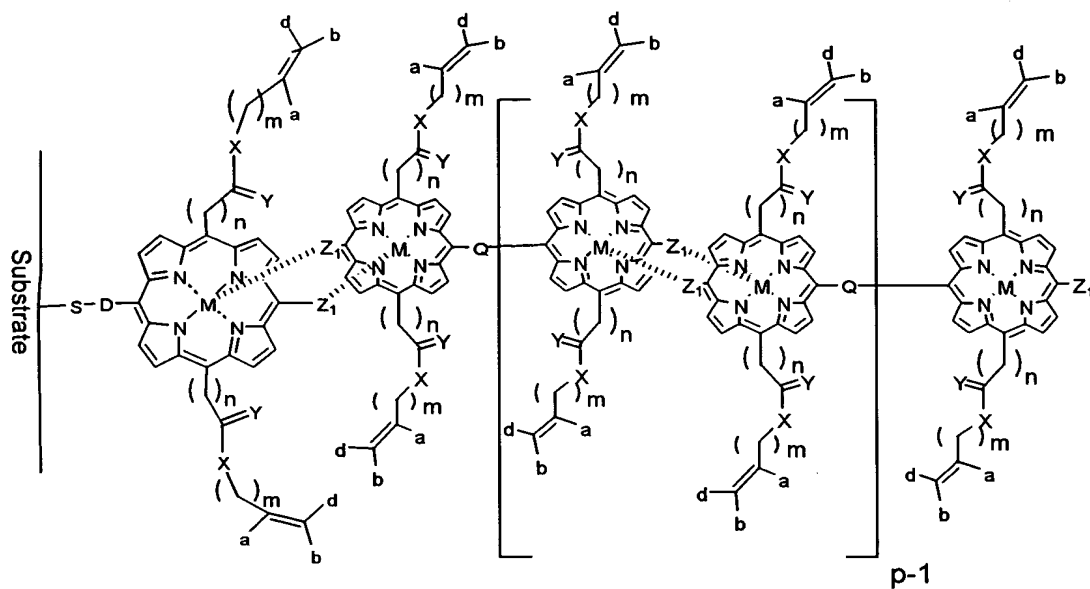

(wherein each of the substituents is as defined above), provided that either one of the fixing a linker molecular and the introducing a metal M may be carried out earlier than the other;

(2) linking the porphyrin residue of the monomolecular film with one of porphyrin residues of meso-meso linked bis-porphyrin represented by the

following formula (III):

(III)

(wherein each of a, b, d, X, Y, m, n, M and Z_1 is as defined above and Q represents a single bond or divalent linking group), via two coordinate bonds, thereby obtaining a first laminate represented by the following formula (IV) or (IV'):
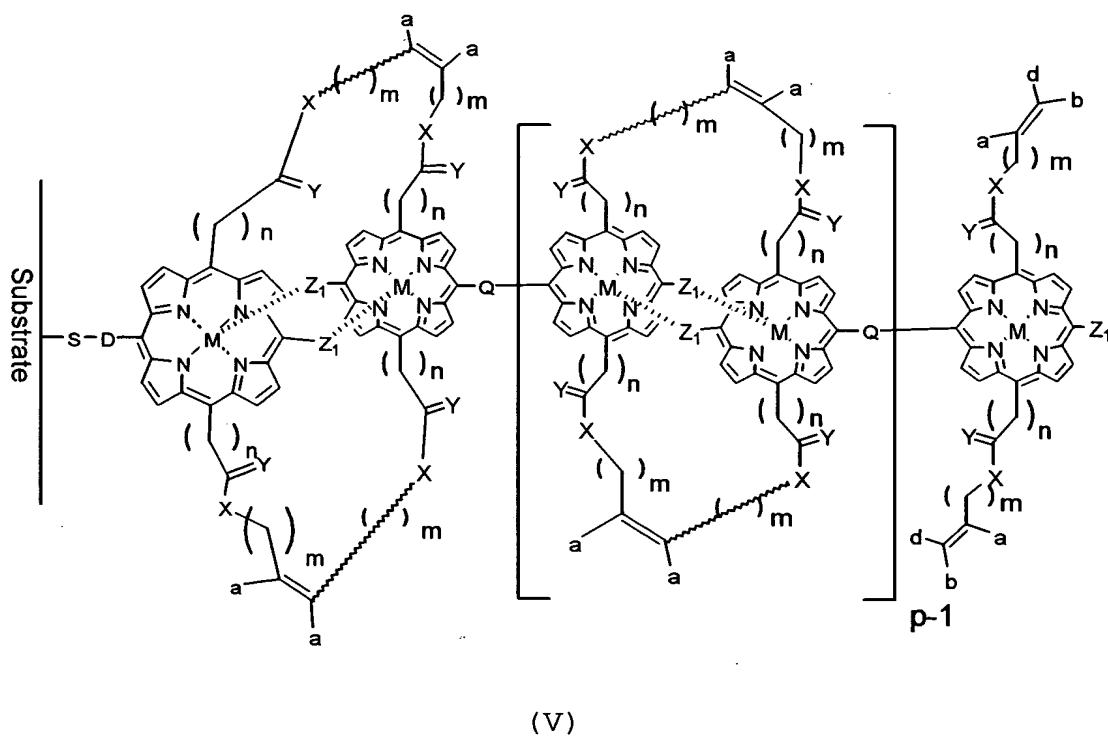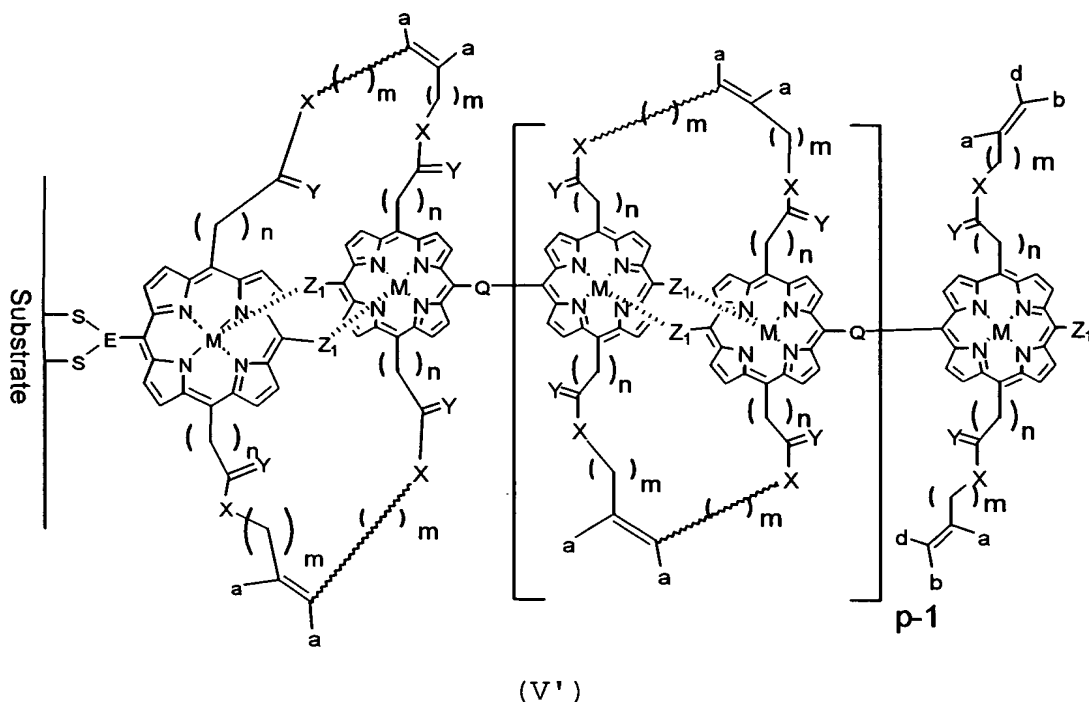
(IV)

(IV')

(wherein each of the substituent is as defined above, and p is 1);

(3) effecting, in the presence of a Grubbs catalyst, a ring-closing metathesis reaction of the olefin portions of the porphyrin residue derived from

the linker molecule, with the corresponding olefin
portions of the porphyrin residue that is coordinated
to the linker molecule, so that the porphyrins are
fixed to each other by covalent bonds, thereby
obtaining a fixed first laminate represented by the
following formula (V) or (V'):

(V)

(V')

(wherein each of the substituents is as defined above,

5   and p is 1);

        (4) optionally,

        linking the porphyrin residue at the terminal end

of the fixed first laminate with one of the porphyrin

residues of another meso-meso linked bis-porphyrin

10   represented by the formula (III), via two coordinate

bonds, in the same manner as in above (2), thereby

obtaining a second laminate represented by the above

formula (IV) or (IV'), wherein p represents an integer

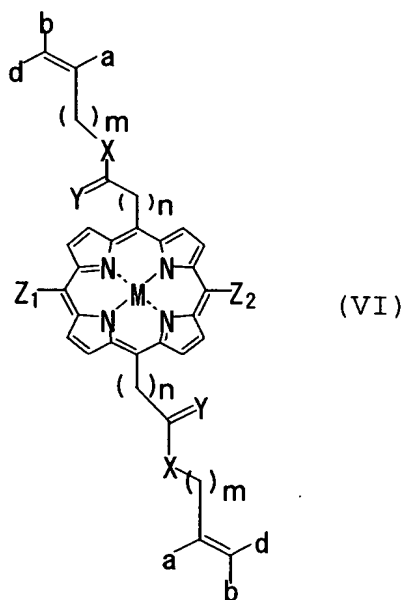of 2 or more); and

15   effecting, in the presence of a Grubbs catalyst,

a ring-closing metathesis reaction in the same manner

as in above (3), thereby obtaining a fixed second

laminate represented by the formula (V) or (V'),

wherein p represents an integer of 2 or more);

wherein the linking and the effecting the ring-closing metathesis reaction, as a cycle, are sequentially repeated q times, thereby obtaining a fixed q^{th} laminate represented by the formula (V) or (V'), wherein p represents q, and q is an integer of 2 or more;

(5) linking the porphyrin residue at the terminal end of the fixed first laminate obtained in above (3) or the fixed q^{th} laminate obtained in above (4), with the porphyrin residue of a porphyrin derivative represented by the following formula (VI):

(VI)

(wherein each of Z_1, M, X, Y, m, n, a, b and d is as defined above, and Z_2 represents a group having a functional group which can be an electron acceptor or electron donor, or a group which can be the terminal group of the porphyrin polymer), via two coordinate

bonds, thereby obtaining a photo-functional molecule precursor represented by the following formula (VII) or (VII'):

(VII)

(VII')

Substrate
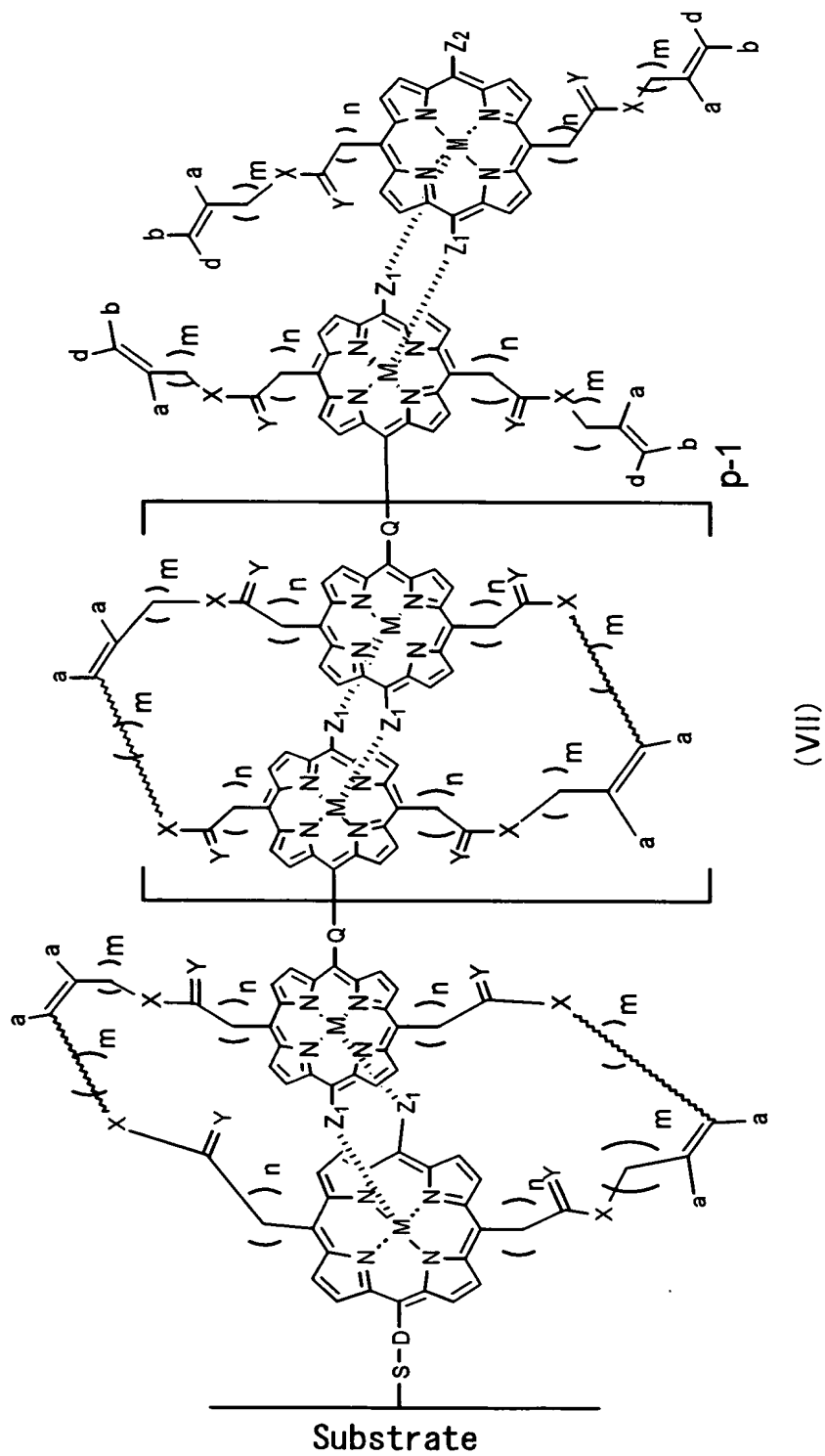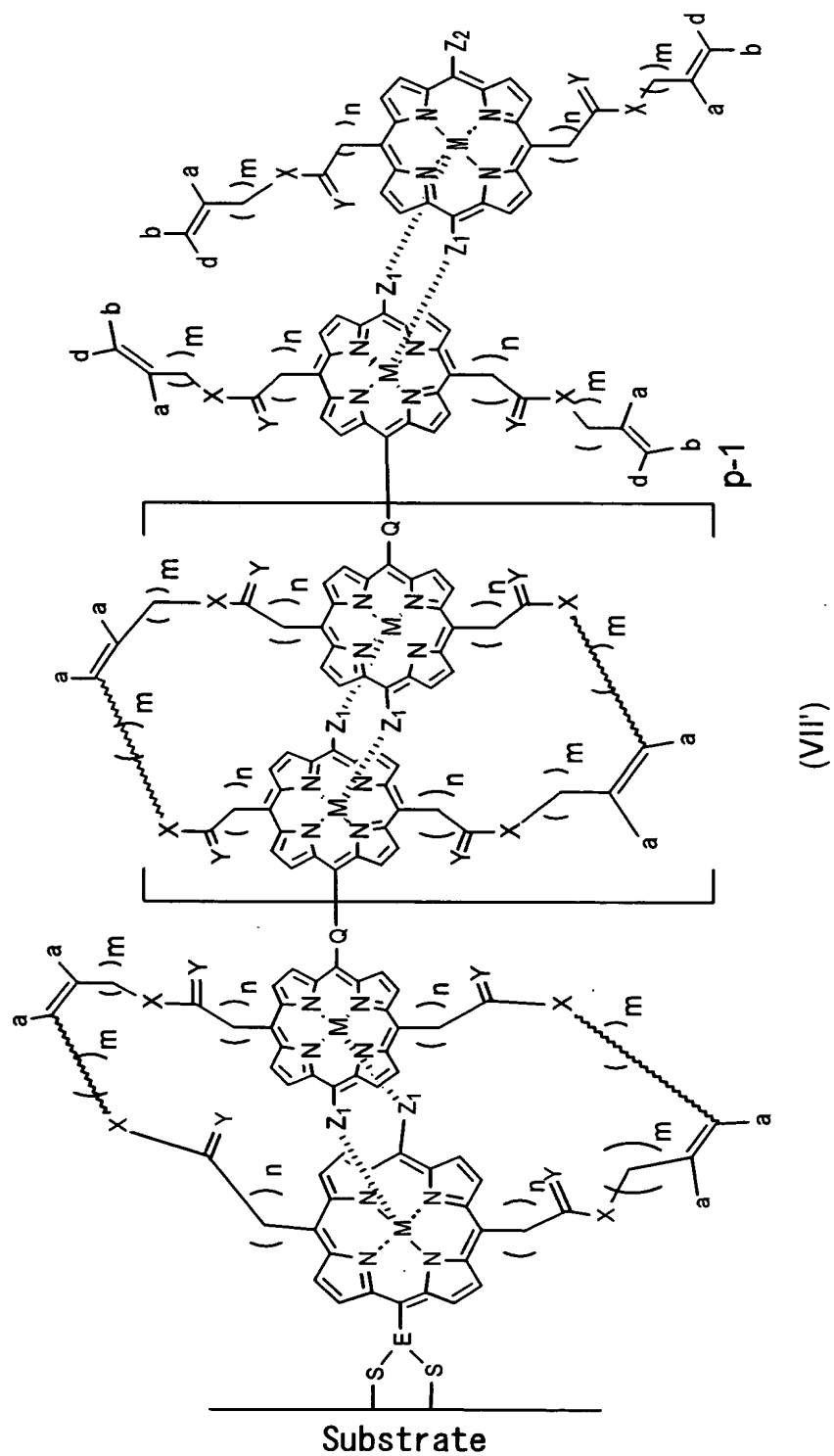
(wherein each of the substituents is as defined above);
and

(6) effecting, in the presence of a Grubbs
catalyst, a ring-closing metathesis reaction of the
olefin portion derived from the porphyrin derivative
represented by the formula (VI), with the olefin
portion of the porphyrin residue that is coordinated to
the porphyrin derivative, so that the porphyrins are
fixed to each other by covalent bonds, thereby
obtaining a photo-functional molecule element
represented by the following formula (VIII) or (VIII'):

(VIII)

(VIII')
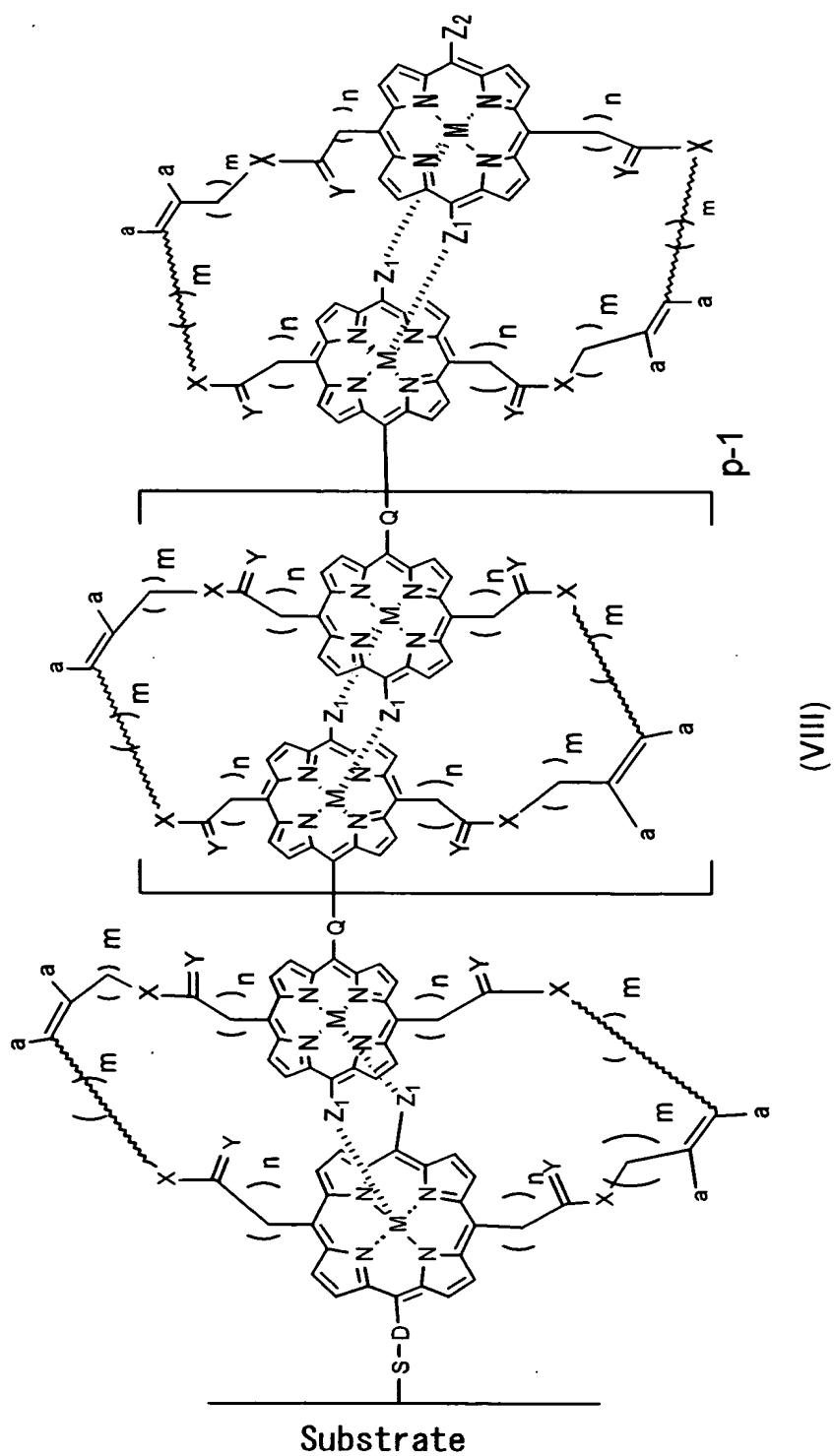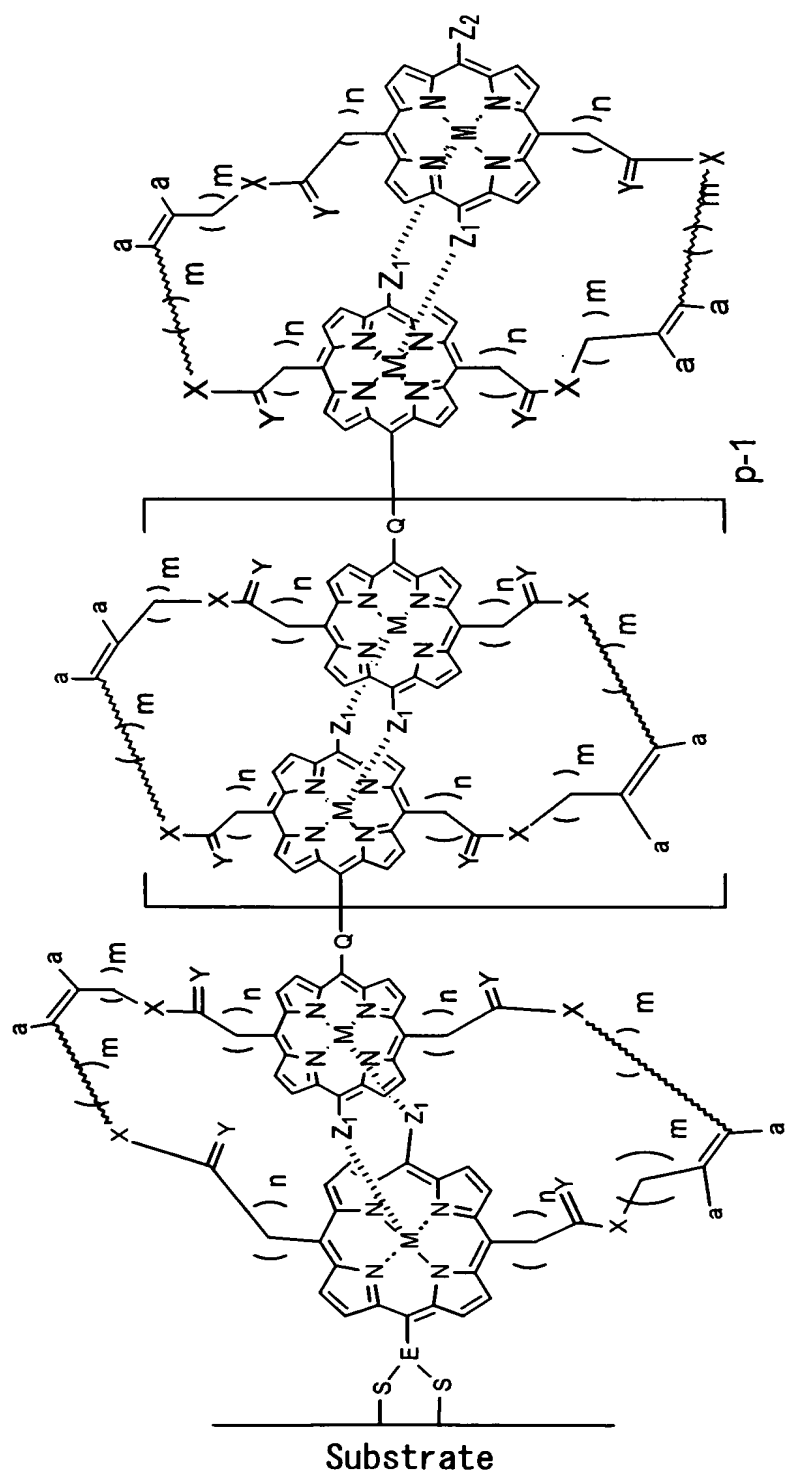
(wherein each of the substituents is as defined above).

Additional objects and advantages of the invention will be set forth in the description which follows, and in part will be obvious from the description, or may be learned by practice of the invention. The objects and advantages of the invention may be realized and obtained by means of the instrumentalities and combinations particularly pointed out hereinafter.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

The accompanying drawings, which are incorporated in and constitute a part of the specification, illustrate presently preferred embodiments of the invention, and together with the general description given above and the detailed description of the preferred embodiments given below, serve to explain the principles of the invention.

FIG. 1 is a graph showing absorbance at each cycle (totally 5 cycles) required for obtaining Zn-SAM F-3 and Antenna-ZnSAM/Au F-5.

FIG. 2 is a schematic view of a device employed in an example, in which device a triple-pole electrochemical cell is combined with an optical cell.

FIG. 3 is a graph showing results of photocurrent measurement of Zn-SAM F-3 (white and black squares indicate photocurrent and dark current, respectively) and C60-ZnSAM/Au F-4 (white and dark circles indicate photocurrent and dark current, respectively).

FIG. 4 is a graph showing results of photocurrent measurement of Zn-SAM F-3 (white and black triangles indicate photocurrent and dark current, respectively), Antenna-ZnSAM/Au F-5 (white and black squares indicate photocurrent and dark current, respectively) and C60-Antenna-ZnSAM/Au F-6 (white and dark circles indicate photocurrent and dark current, respectively).

FIG. 5 is a graph showing results of photocurrent measurement of Antenna-ZnSAM/Au F-5 (white and black circles indicate photocurrent and dark current, respectively).

DETAILED DESCRIPTION OF THE INVENTION

First, the photo-functional molecule element in which covalently-fixed porphyrin polymer is laminated on a support, and represented by the formula (VIII) or (VIII') will be described in detail.

In the formula (VIII), a represents H, an alkyl group or aryl group. A plurality of a's may be the same or different. A plurality of a's are preferably the same, in light of making the preparation process simple.

The alkyl group herein indicates a normal, branched or cyclic monovalent saturated aliphatic group (hereinafter, when a substituent is an alkyl group, the same principle as described above will be applied thereto). The aryl group indicates a monovalent aromatic hydrocarbon group, which may either be a

monocyclic or condensed ring of two or more rings
(hereinafter, when a substituent is an aryl group,
the same principle as describe above will be applied
thereto). Further, the alkynyl group represents a

5   normal, branched or cyclic unsaturated aliphatic group.
The above-described alkyl group, alkynyl group and aryl
group may have a substituent, when it is possible to
do so (hereinafter, this principle is also applied to
a group other than the alkyl group and the aryl group).

10   The number of carbon atoms of the alkyl group
represented by a may be determined in consideration of
whether or not the double bond between the carbon atom
to which one a is bonded and the carbon atom to which
another a is bonded, can serve for a ring-closing

15   metathesis reaction, whether or not a compound as a raw
material of the alkyl group can be synthesized easily,
and/or the function which the synthesized product is
expected to have. The number of carbon atoms of the
alkyl group is generally 1 to 8, and preferably 1 to 2.

20   The number of carbon atoms of the aryl group
represented by a may be determined from the same
viewpoint as described above. The number of carbon
atoms of the aryl group represented by a is generally
in a range of 6 to 20 (e.g., phenyl, naphthyl,

25   anthracenyl, pyrenyl, naphthacenyl), and preferably in
a range of 6 to 10.

In the general formula (VIII), X represents $-O-$,

$-S-$, $> NR_{101}$ (wherein R_{101} represents H or an alkyl group), CH_2 or single bond.

The number of carbon atoms of the alkyl group represented by R_{101} is not particularly restricted, but is generally in a range of 1 to 4.

In the general formula (VIII), X is preferably $-O-$ in light of the easiness in synthesis of the raw material compound and the function expected for the synthesized product.

In the general formula (VIII), Y represents $=O$, $=S$ or 2H. Here, the expression that "Y represents 2H" indicates a state in which each of two hydrogen atoms is bonded, by single bond, to a carbon atom to which Y is bonded.

Y is preferably $=O$ in light of the easiness in synthesis of the raw material compound and the function expected for the synthesized product.
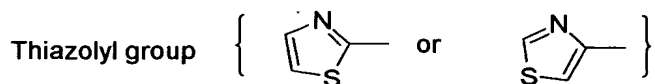
In the general formula (VIII), m represents an integer of 0 to 4. m is preferably 1 in light of the easiness in synthesis of the raw material compound and the function expected for the synthesized product.
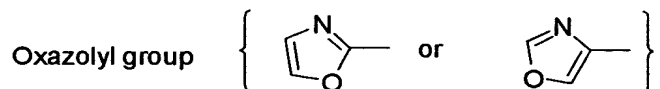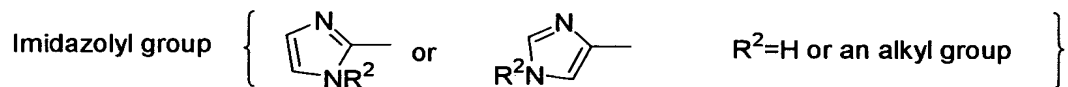
In the general formula (VIII), n represents an integer of 0 to 6. n is preferably 2 in light of the easiness in synthesis of the raw material compound and the function expected for the synthesized product.

In the general formula (VIII), Z_1 represents a 5- or 6-membered nitrogen-containing heteroaromatic ring

group capable of forming a coordination bond. A "5- or
6-membered nitrogen-containing heteroaromatic ring
group capable of forming a coordination bond" indicates
a 5- or 6-membered heterocycle containing at least one
nitrogen atom therein, and the type thereof is not
particularly restricted as long as the heterocycle has
aromaticity. The heterocycle may include oxygen,
sulfur or the like as a hetero atom other than
nitrogen. In a case in which a structural isomer of
the nitrogen-containing heteroaromatic ring group
exists, such a structural isomer is included to Z_1.

Examples of the 5- or 6-membered nitrogen-
containing heteroaromatic ring group include imidazolyl
group, oxazolyl group, thiazolyl group and pyridyl
group shown below, but the heteroaromatic ring is not
limited to these:

Imidazolyl group $\left\{ \vphantom{\begin{array}{c}a\\b\end{array}} \right.$ or R^2=H or an alkyl group $\left. \vphantom{\begin{array}{c}a\\b\end{array}} \right\}$

Oxazolyl group $\left\{ \vphantom{\begin{array}{c}a\\b\end{array}} \right.$ or $\left. \vphantom{\begin{array}{c}a\\b\end{array}} \right\}$

Thiazolyl group $\left\{ \vphantom{\begin{array}{c}a\\b\end{array}} \right.$ or $\left. \vphantom{\begin{array}{c}a\\b\end{array}} \right\}$

2-pyrizyl group

In the above-described imidazolyl group, the number of carbon atoms of the alkyl group represented by R^2 is generally in a range of 1 to 10, and preferably 1 or so in light of the easiness in

5   synthesis of the raw material compound and the function expected for the synthesized product.

In the general formula (VIII), Z_1 is preferably imidazolyl group in light of the strength of bond between Z_1 and the core metal of the porphyrin metal

10   complex.

In the general formula (VIII), Z_2 represents a group having a functional group which can be an electron acceptor or electron donor, or a group which can be the terminal group of the porphyrin polymer.

15   Specific examples of the group having a functional group which can be an electron acceptor, represented by Z_2, include the following groups:
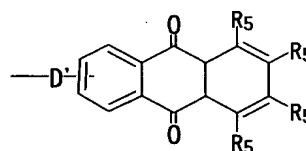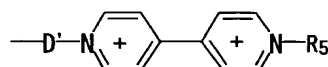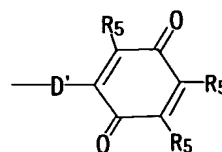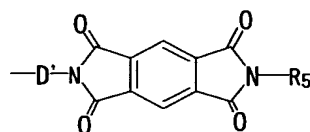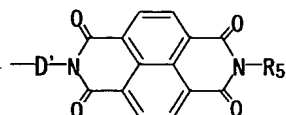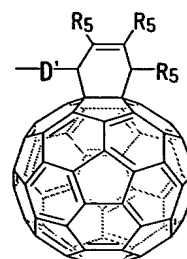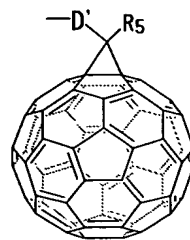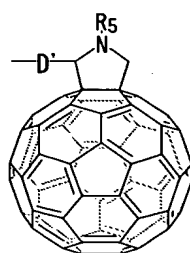
[(wherein D' represents, in addition to those defined as D of the general formula (VIII), a single bond,
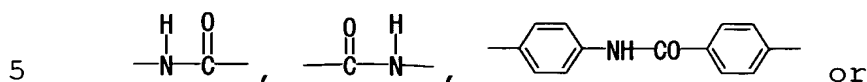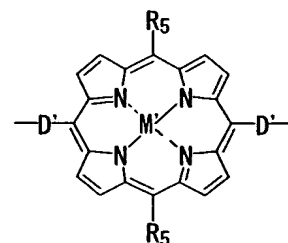
(wherein R5 represents H, an alkyl group, aryl group, halogen atom, cyano group or alkoxy group. Two R5s may be the same or different. M' represents 2H or an ion of the metal selected from typical metals and transition metals represented by M)], but the group having a functional group which can be an electron acceptor is not limited to these. For example, a group capable of receiving an electron from excited porphyrin

(such as a metal complex whose energy level of reduction potential is lower than that of excited porphyrin) can be a group having a functional group which can be an electron acceptor.

Examples of the group that can be the terminal group of porphyrin polymer, and represented by Z_2, include an alkyl group, aryl group and alkynyl group. The number of the carbon atoms of the alkyl group and that of the aryl group are the same as described above for the substituent represented by a. In a case in which the group represented by Z_2 is alkynyl group, the number of carbon atom of the Z_2 group may be in a range of 2 to 18, and preferably 2 or so.

In a case in which the group represented by R_5 is an alkyl group, aryl group or alkoxy group, the number of carbon atoms of the R_5 group is defined in the same manner as described above. The alkyl portion of the alkoxy group is defined in the same manner as described with regards to the aforementioned substituent represented by a. In a case in which the group represented by R_5 is a halogen atom, specific examples of the halogen atom include F, Cl, Br, I and the like.

Specific examples of the group having a functional group which can be an electron donor, represented by Z_2, include the following groups:
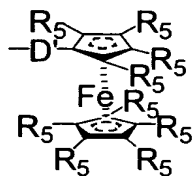
[wherein D' represents, in addition to those defined as D of the general formula (VIII), a single bond,
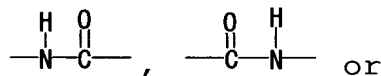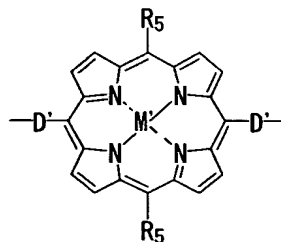
(wherein R_5 represents H, alkyl group, aryl group, halogen atom, cyano group or alkoxy group. Two R_5s may be the same type or different. M' represents 2H or an ion of the metal selected from typical metals and transition metals represented by M)], but the group having a functional group which can be an electron donor is not limited to these examples. For example, a group capable of donating an electron to oxidized porphyrin (such as a metal complex whose energy level
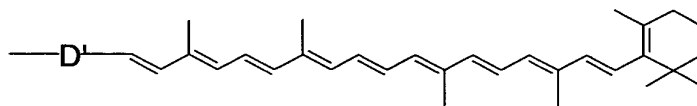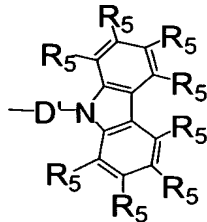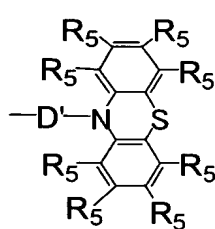
of oxidation potential is higher than that of one electron-oxidized porphyrin) can be a group having a functional group which can be an electron donor.

In the formula (VIII), D represents a divalent group including at least one of arylene group and alkylene group. E represents a trivalent group including at least one of arylene group and alkylene group. R^3 represents H or an acetyl group.

The above-described "divalent group including at least one of arylene group and alkylene group" represented by D indicates a divalent group having arylene group and/or alkylene group at terminal ends thereof, and between which terminal end groups, at least one group such as ether group, carbonyl group and functional group having a hetero atom (e.g., an ester group, and amido group) intervenes, but such intervening group may not exist. The intervening group(s) located between the two terminal end groups is a group that can be used for linking a porphyrin ring with a sulfur atom-containing group when a linker molecule is synthesized. The number of carbon atoms of the arylene group and alkylene group is not particularly restricted, but is generally in a range of 1 to 18 for the alkylene group and in a range of 6 to 13 for the arylene group.

The above-described "trivalent group including at least one of arylene group and alkylene group"

represented by E indicates a group obtained by removing
one hydrogen atom from the aforementioned group
represented by D.

In the formula (VIII), M represents an ion of
a metal selected from the group consisting of typical
metals and transition metals. Here, the "typical
metals" represent metals which belong to 1A, 2A, 2B, 3B
to 7B and 0 groups on the periodic table, and specific
examples thereof include Mg, Zn, Cd, Hg, Al, Ga, In,
Tl, Si, Ge, Sn, Pb, P, As, Sb, Bi and the like. The
"transition metals" represent metals which belong to 3A
to 7A, 8 and 1B groups, and specific examples thereof
include Sc, Y, lanthanoid (La, Ce, Pr, Nd, Pm, Sm, Eu,
Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), Ti, Zr, Hf, V, Nb, Ta,
Cr, Mo, W, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd,
Pt, Cu, Ag, Au and the like. The valence number of
these metals is not particularly restricted, as long as
the metals can serve as the core metal of a porphyrin
metal complex. The valence number of these metals is
generally divalent or trivalent.

The metal represented by M is not particularly
restricted, as long as coordinate bond can be formed
between M and the above-described Z. The metal
represented by M is preferably Zn, Mg, Co or Fe, in
light of the reactivity, strength of the coordinate
bond, and the function which the synthesized product is
expected to effect.

In the formula (VIII), Q represents single bond or a linear divalent linking group. The type of the linear divalent linking group may be determined in consideration of the function which the synthesized product is expected to effect (e.g., conductivity of electron or energy, strength of bond between porphyrin rings, capacity of maintaining a steric configuration).

Herein, the linear, divalent linking group includes: (a) a divalent linking group whose connecting bonds at both ends thereof are aligned on the same line; or (b) a divalent linking group whose connecting bonds at both ends thereof are aligned in parallel with each other. Here, the expression that the connecting bonds at both ends of the divalent linking group are "aligned on the same line" does not necessarily mean that the connecting bonds are aligned on the same, geometrically perfect line. Similarly, the expression that the connecting bonds at both ends of the divalent linking group are "aligned in parallel with each other" does not necessarily mean that the connecting bonds are aligned in parallel with each other in the geometrically perfect manner. Accordingly, it suffices, as long as the polymer constituted by way of the liner, divalent linking group is not cyclic, but takes on the substantially linear chain-like form as a whole. In particular, in the case in which the polymer formed by way of the liner, divalent linking group is relatively

long, the connecting bonds at both ends of the liner,
divalent group need to be neither aligned on the same,
geometrically perfect line nor aligned in parallel
(with each other) in the geometrically perfect manner.
In this case, a chain-like polymer can reliably be
formed as long as the connecting bonds at both ends of
the liner, divalent group are located substantially on
the same line or aligned substantially in parallel with
each other. Hereinafter, in the present specification,
the state in which the connecting bonds are aligned
substantially on the same line and the state in which
the connecting bonds are aligned substantially in
parallel with each other will simply be referred to as
"linear" and "in parallel", respectively.

Examples of the group (a) whose connecting bonds
at both ends thereof are aligned on the same line
include: a divalent, saturated or unsaturated aliphatic
hydrocarbon group [e.g., alkylene group having 1-3
carbon atoms (e.g., $-CH_2-$), $-C{\equiv}C-$]; a divalent,
saturated or unsaturated hydrocarbon ring group
[e.g., a monocycle or condensed ring having 3-20 carbon
atoms (e.g., 1,3-cyclobutylene (in trans form),
1,4-phenylene, 2,7-pyrenylene); a divalent, saturated
or unsaturated hetero cyclic group [e.g., a 6-membered
hetero cycle containing at least one N, S, O or P atom
or the like as a hetero atom (such as 2,5-pyridine);
and a combination of at least two of the aforementioned

divalent groups. When at least two of the
aforementioned divalent groups are combined, the groups
may be either the same (the resulting structure is what
is called a bis structure) or different. Combining

5   the groups of the same type is preferable, in light of
making the synthesis of the raw material compound easy.
Further, when at least two of the aforementioned
divalent groups are combined, these divalent groups may
be intervened by a group whose connecting bonds at both

10   ends thereof are aligned on the same line, such as -O-
and -C(=O)-. Still further, the divalent groups may
be intervened by any linking group, as long as the
connecting bonds of both ends of the linking group
represented by Q are eventually aligned on the same

15   line.

Examples of the group (b) whose connecting bonds
at both ends thereof are aligned in parallel with each
other include: a divalent, saturated or unsaturated
hydrocarbon group [e.g., linear alkyl groups having 3-5

20   carbon atoms (such as n-propylene), -C=C- (in trans
form)]; a divalent, aromatic hydrocarbon ring group
[e.g., condensed ring having approximately 10-20 carbon
atoms (e.g., 2,6-naphthylenyl and 1,6-pyrenylene)]; and
the like.

25   Further, the aforementioned group (a) whose
connecting bonds at both ends thereof are aligned on
the same line may be combined with the aforementioned

group (b) whose connecting bonds at both ends thereof
are aligned in parallel with each other, as long as the
connecting bonds of the thus formed divalent group are
eventually aligned on the same line or aligned in
parallel with each other.

Specific examples of the divalent linking group
whose connecting bonds at both ends thereof are: (a)
aligned on the same line or (b) aligned in parallel
with each other are described below. It should be
noted, however, that the group represented by Q is not
limited to these.

(a)

2,7-pyrenylene

$-C\equiv C-$ $-C\equiv C-C\equiv C-$

$-C\equiv C-$ $-C\equiv C-$

(b)

1,3-cyclobutylene (*trans*)

-CH=CH(*cis*)j

2,6-naphthylene

1,6-pyrenylene
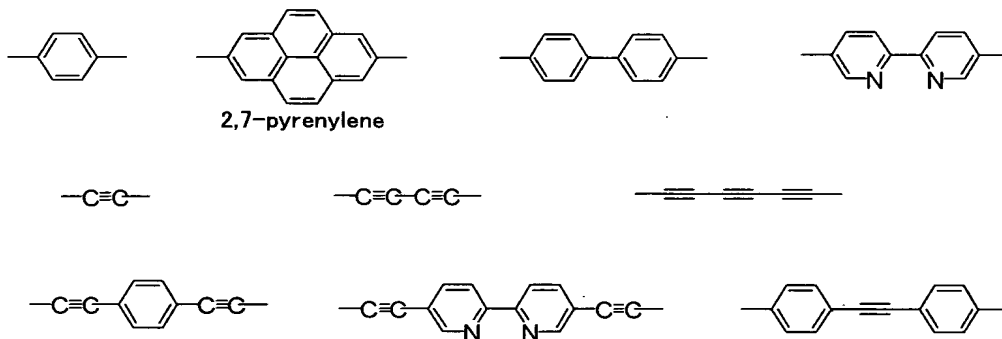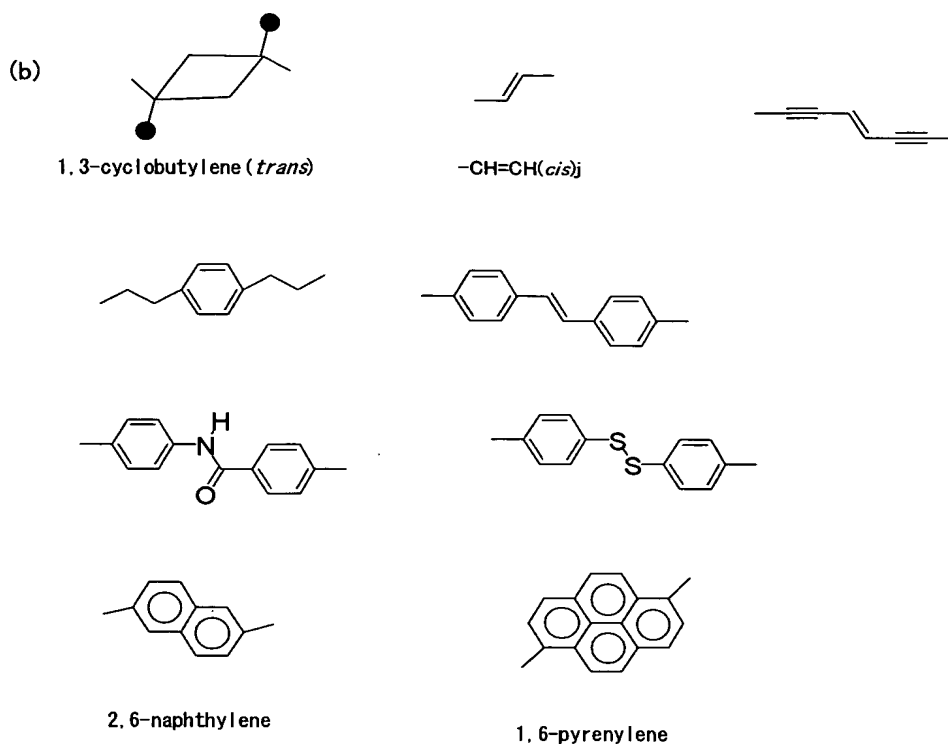
In the formula (VIII), Q is preferably a single
bond or alkynylene group represented by the formula:
$(-C \equiv C-)_n$, wherein n represents an integer of 1 to 3),
in consideration of the strength of the bond,
stability, and easiness of the synthesis of the raw
material.

In the formula (VIII), p represents an integer o 1
or more. The value of p may be selected in an
appropriate manner, in accordance with the application
of the photo-functional molecule element of the present
invention. The upper limit of the p value is not
particularly restricted, and it is assumed that the
photo-functional molecule element whose p value is
approximately 10,000 could be produced. At the present
stage, the photo-functional molecule element whose p · ·   · · · · · ·

value is approximately 100 can be produced.

The photo-functional molecule element represented by the formula (VIII) includes a photo-functional molecule element in which two or more types of porphyrins are laminated and fixed in a desired order. For example, the photo-functional molecule element represented by the formula (VIII) can be made a gradient-functional material having a gradient of potential, by fixing stepwise porphyrin polymers which are different in energy level as shown in the schematic view set forth below:

Linker porphyrin

Solid substrate

Self-organization & fixation

Self-organization & fixation

Self-organization & fixation

Photoelectric element having a gradient of energy level

High

Energy level

Low
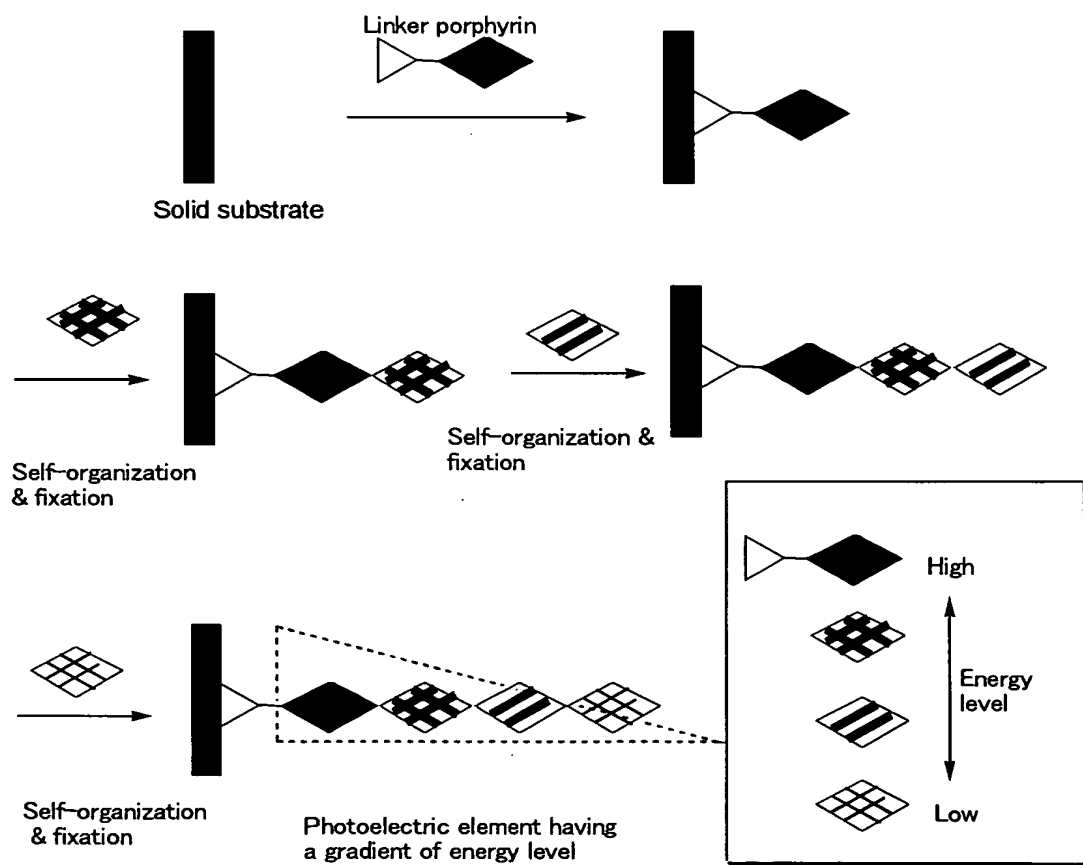
As a result, the direction in which an electron and a hole flow can be controlled (i.e., rectification can be effected). Since transfer of photo-excited electrons is caused in each of the porphyrins as the

5   structural unit, the photo-functional molecule of the formula (VIII) can be used as a photo-functional molecule element. Specifically, it has already been confirmed that the thus produced element functions as a photoelectric conversion element (refer to example 3).

10   In the formula (VIII), examples of a metal material which can be used as the substrate include, apart from gold, a metal having good conductivity such as silver, copper, platinum, palladium, nickel, aluminum, and a material obtained by vapor-depositing

15   one of these metals on a solid substrate (e.g., slide glass, mica, silicon wafer) such that the thickness of the metal is generally 50 to 1000 Å. Also, semiconductor including TiO_2, SnO_2, ITO (indium tin oxide), CdS, CdSe, GaAs, GaP, Si, InP, CdTe, and a

20   semiconductor obtained by adding an electron acceptor or electron donor to one of the above-described semiconductors so that the band structure thereof is changed, may be used as the substrate. Also, organic solid substrate including macromolecular polymers of

25   various types and an organic solid substrate obtained by coating one of these polymers on a solid substrate such that the thickness of the polymer is generally 50

to 1000 Å, may be used as the substrate. Conductive or semiconductive polymer (PPV, i.e., polyphenylenevinylene-type polymer), P3OT (polythiophene-type polymer), polypyrrole-type polymer, polyacetylene-type polymer, polydiacetylene-type polymer, in particular, are especially promising because these polymers can construct a completely organic element by being combined with a porphyrin element.

Although the formula (VIII) set forth above shows a state in which a porphyrin chain extends from a substrate by way of a single -S- bond, the photo-functional molecule element of the present invention is generally formed on the substrate so as to expand thereover as a film. In one example, in a case in which gold is used as the substrate, the surface-coating rate calculated by the Au-S reductive elimination method is approximately 7×10^{13} molecule/cm^2 (10^{-10} mol/cm^2). That is, the area of the gold substrate occupied by one molecule thereon is approximately 3 nm^2/molecule. As the width of the porphyrin ring is approximately 1 nm, it is understood that the film is formed on the substrate quite densely.

In the formula (VIII) set forth above, the porphyrin chain extends in a direction of normal line to the substrate surface. It should be noted, however, that the angle formed between the porphyrin chain and

the substrate surface in the formula (VIII) does not necessarily reflect an angle actually formed in practice. In consideration of the above-described assumption from the data of the area occupied by one porphyrin molecule that the porphyrin molecules are densely arranged and a fact that the structure of the porphyrin chain properly extends, it is assumed that the porphyrins are bonded to the substrate surface so as to stand on the substrate surface, with an angle in a certain range formed therebetween.

The photo-functional molecule element represented by the formula (VIII') is different from the photo-functional molecule element represented by the formula (VIII) in that the linker molecule is bonded to the substrate by way of two sites, but the former shares the same definitions of the substituents and the like as the latter. In the photo-functional molecule element represented by the formula (VIII'), the laminated porphyrins are fixed on the substrate more firmly than the photo-functional molecule element represented by the formula (VIII) are because the linker molecule of the former is bonded to the substrate by way of two sites. The photo-functional molecule element represented by the formula (VIII') has an advantage that porphyrins thereof are less likely to peel off in the soaking and washing processes for extending the porphyrin polymer. For example, in the

case of the photo-functional molecule element

represented by the formula (VIII) in which the

laminated porphyrins are bonded to the substrate by way

of one site, the absorption attributed to porphyrin may

5   decrease by approximately 50 % due to the soaking and

washing processes. In contrast, in the case of the

photo-functional molecule element represented by the

formula (VIII'), it is assumed that the porphyrins

are less likely to peel off and thus the magnitude of

10   a decrease in the absorption attributed to porphyrin is

relatively small.

Next, the method of producing the photo-functional

molecule element represented by the formula (VIII)

or the formula (VIII') will be described in detail.

15   In the following descriptions, each of the substituents

has the same manner as described above, unless

otherwise specified.

The method of producing the photo-functional

molecule element represented by the formulae (VIII) or

20   (VIII') includes the processes (1) to (6) set forth

below.

(Process 1): A step of fixing, on a substrate,

a linker molecule represented by the following

formula (I):

(I)

[wherein a, b and d independently represent H, an alkyl group or aryl group; X represents $-O-$, $-S-$, $> NR_{101}$

5   (wherein R_{101} represents H or an alkyl group), CH_2 or single bond; Y represents $=O$, $=S$ or 2H; m represents an integer of 0 to 4; n represents an integer of 0 to 6; Z_1 represents a 5- or 6-membered nitrogen-containing heteroaromatic ring group capable of forming a

10   coordination bond; and R^1 represents

(wherein D represents a divalent group including at least one of arylene group and alkylene group;

15   E represents a trivalent group including at least one

of arylene group and alkylene group; and R^3 represents

H or an acetyl group)]; and

a step of introducing a metal M selected from the

group consisting of typical metals and transition

metals to the porphyrin residue derived from the linker

molecule,

thereby obtaining a monomolecular film represented

by the following formula (II) or (II'):

(II)   (II')
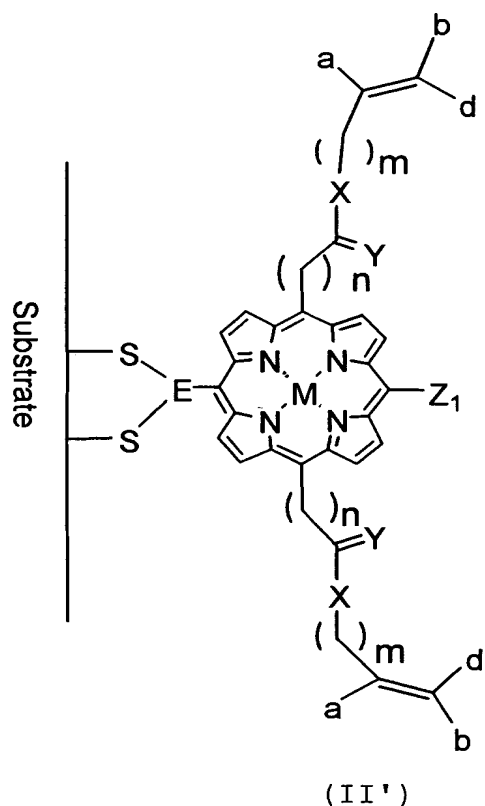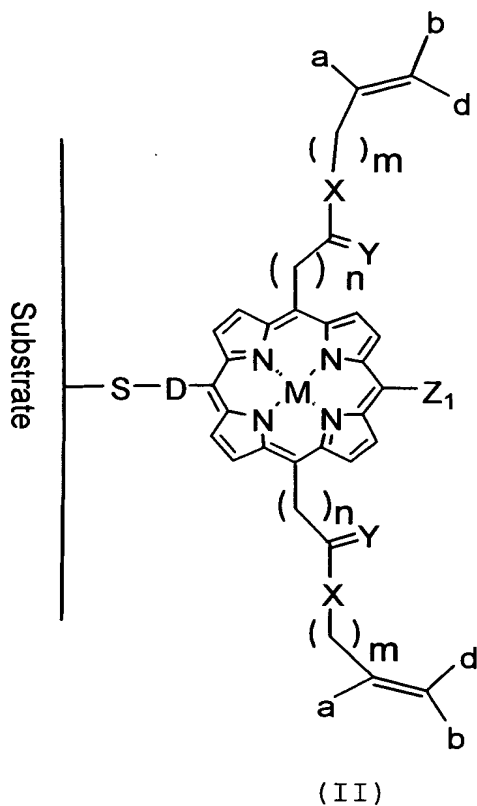
(wherein each of the substituents is as defined above).

In the process (1), either one of the step of

fixing the linker molecule on the substrate and the

step of introducing the metal M to the porphyrin

residue may be carried out earlier. In other words,

the order of these two steps may be reversed. However, fixing the linker molecule on the substrate first and then introducing the metal M thereto results in a better monomolecular film and thus is preferable.

5   The substrates, e.g., the substrate on which gold or the like has been vapor-deposited, are commercially available or can be prepared from a commercial product by the method disclosed in literatures.

The linker molecule can be fixed on a substrate

10   by soaking (generally overnight) the substrate in a solution of the linker molecule. Examples of the solvent of the linker molecule solution include CH_2Cl_2, chloroform, bromobenzene, methanol or pyridine, but the solvent is not limited to these. Any solvent that

15   dissolves the linker molecule and is adaptable to the substrate may be used. Even a polar solvent may be used, because the bond between the linker molecule and the substrate is so strong that the bond is maintained in a polar solvent.

20   The metal M can be introduced into the porphyrin ring by soaking (generally for 60 to 120 minutes) the substrate having the linker molecule fixed thereon in a solution of a salt (e.g., an acetate or hydrochloride) of the metal to be introduced. Example of the solvent

25   is $CHCl_3$ and/or methanol, but the solvent is not limited to these. Any solvent that dissolves the metal salt and is miscible with porphyrin may be used.

During this process, it is preferable that the mixture
is heated so that the temperature thereof is increased
to about 40 to 50°C. In a case in which the metal M is
introduced to the porphyrin ring prior to fixing the
linker molecule on a substrate, the metal M can be
introduced into the porphyrin ring in a condition
similar to that described above.

The monomolecular film obtained by the process (1)
and represented by the formula (II) or the formula
(II') is washed, if necessary, and then the next
process (2) is carried out thereto. Examples of the
solvent which can be used in the washing process
include methanol, hexane, CH_2Cl_2, but the solvent for
washing is not limited to these. A washing process
similar to that described above may be carried out
between the processes described below.

Process (2): A step of linking the porphyrin
residue of the monomolecular film with one of porphyrin
residues of meso-meso linked bis-porphyrin represented
by the following formula (III):

(III)

(wherein each of a, b, d, X, Y, m, n, M and Z_1 is as defined above and Q represents a single bond or divalent linking group), via two coordinate bonds, thereby obtaining a first laminate represented by the following formula (IV) or (IV'):

(IV)

(IV')
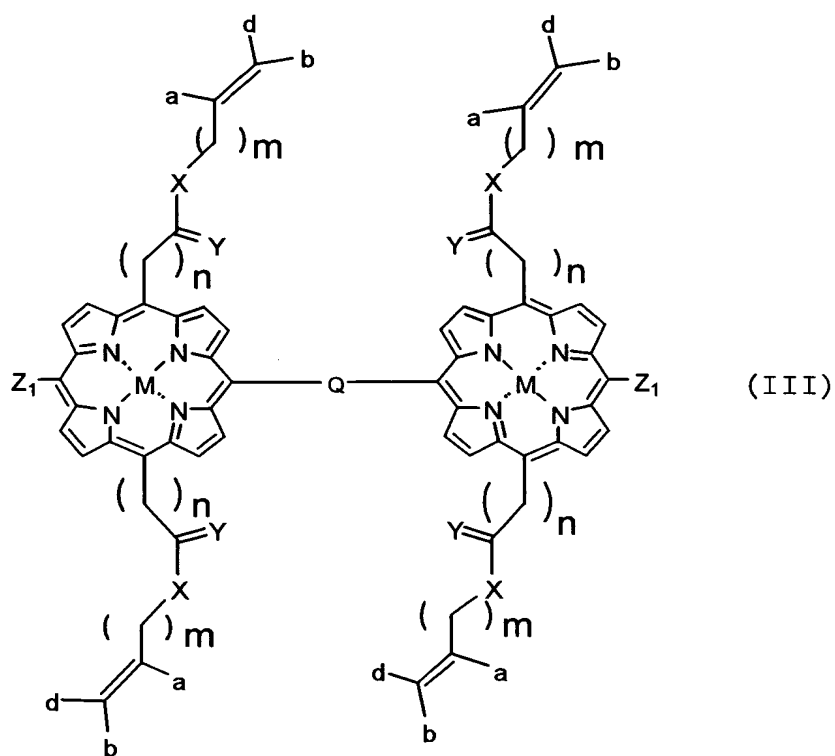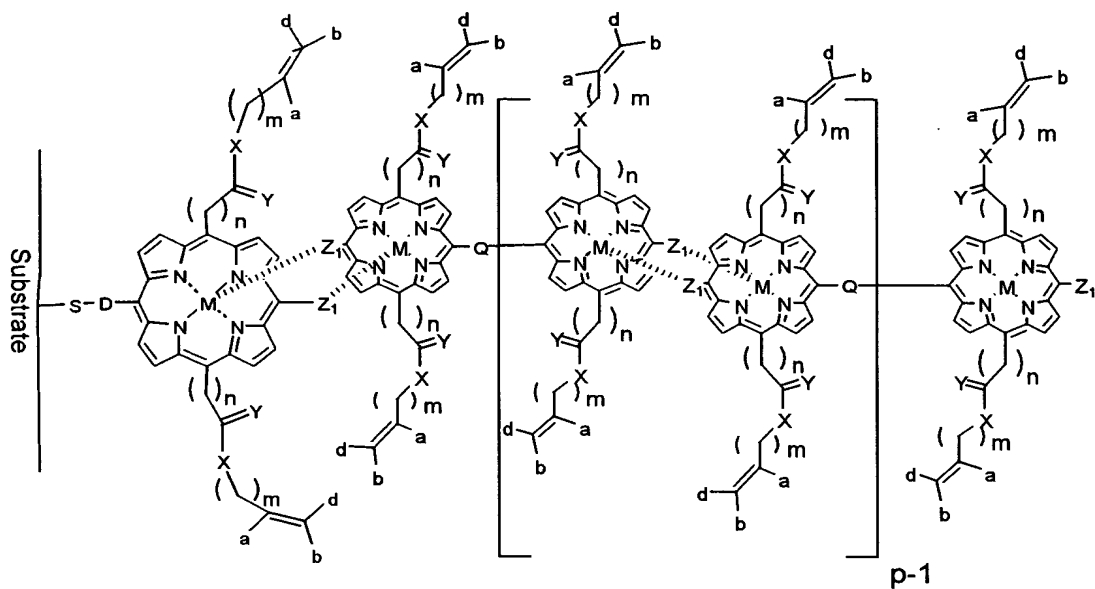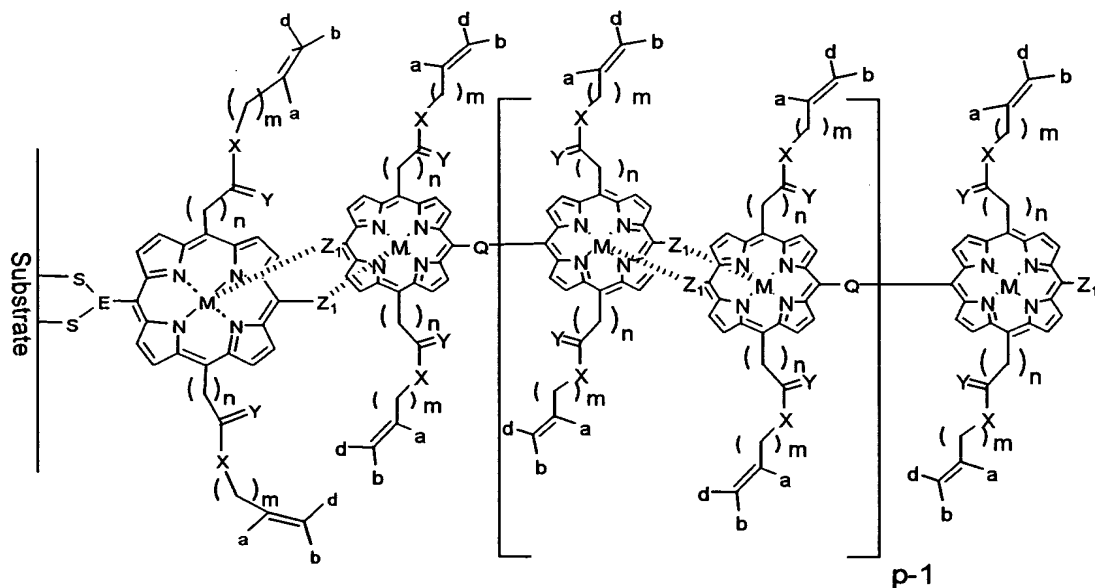
(wherein each of the substituent is as defined above,
and p is 1).

In the process (2), the first laminate is

obtained by soaking (generally, for 1 to 5 hours)

the monomolecular film obtained by the process (1) in

a solution of the meso-meso linked bis-porphyrin represented by the formula (III). The solvent that may be used is chloroform or CH_2Cl_2 containing approximately 20 mM pyridine. In the solvent mixture,

5 the use of 20 mM pyridine renders the meso-meso linked bis-porphyrin partially dissociated, thereby to make the meso-meso linked bis-porphyrin a short unit, as short as almost a monomer. If no pyridine is used, meso-meso linked bis-porphyrin forms a large polymer

10 and does not extend on the substrate. On the other hand, if the concentration of pyridine in the solvent mixture is higher than 20 mM, the meso-meso linked bis-porphyrin does not form coordination bonds with the porphyrin that has been attached to the substrate,

15 i.e., the polymer does not extend. It should be noted, however, that other solvent mixture having a proper concentration which exhibits the similar characteristics mentioned above may be used.

Process (3): A step of effecting, in the presence

20 of a Grubbs catalyst, a ring-closing metathesis reaction of the olefin portions of the porphyrin residue derived from the linker molecule, with the corresponding olefin portions of the porphyrin residue that is coordinated to the linker molecule, so that the

25 porphyrins are fixed to each other by covalent bonds, thereby obtaining a fixed first laminate represented by the following formula (V) or (V'):

5

(V)

(V')
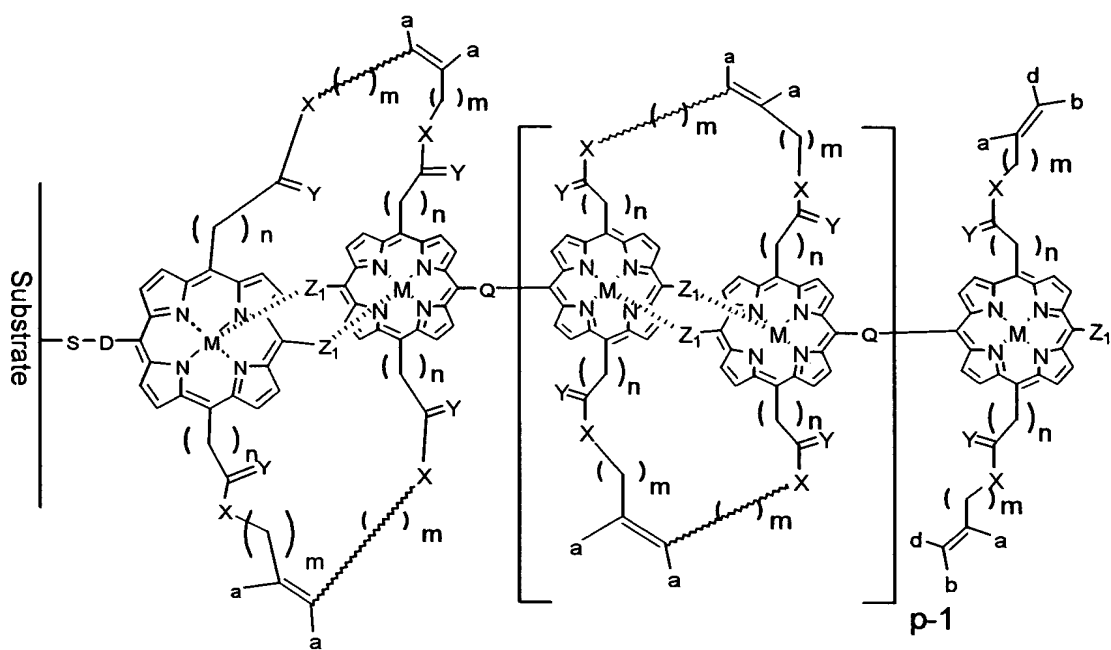
(wherein each of the substituents is as defined above, and p is 1).
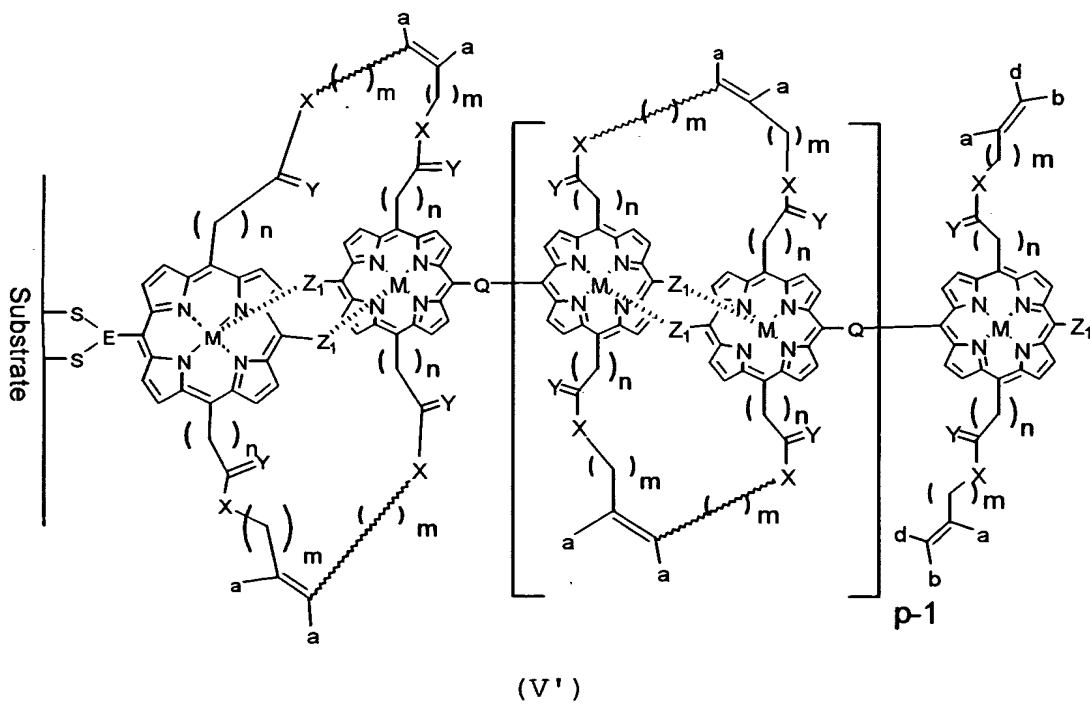
The "Grubbs catalyst" used in the process (3)
generally represents a ruthenium carbene complex
developed by Grubbs et al., which facilitates an olefin
metathesis reaction. When this complex is used, even
in a case in which an olefin compound having various
functional groups such as ester, ketone and amide is
employed as a reaction substrate, the metathesis
reaction selectively proceeds only at the olefin
portion (refer to the general theory by Grubbs et al.
(T. M. Trnka, R.H. Grubbs, Acc. Chem. Res. 34,
18 (2001))).

The ring-closing metathesis reaction in the
process (3) can be effected by soaking (generally for 5
to 20 minutes) the first laminate obtained in the
process (2) in a solution (example of the solvent is a
hydrocarbon-based solvent, such as chlorohydrocarbon
solvent (CH_2Cl_2 or chloroform)) of Grubbs catalyst.
It is preferable that this reaction is carried out
in inactive atmosphere such as nitrogen or argon.
The reaction, however, proceeds in air without causing
any problem.

The ring-closing metathesis reaction of the
process (3) occurs between the olefin portion of the
porphyrin residue derived from the linker molecule
of the first laminate and the olefin portion of the
porphyrin residue linked, by coordinate bond, with the
porphyrin residue derived from the linker molecule.

The ring-closing metathesis reaction of the process (3) does not occur between the meso-meso linked bis-porphyrin of the formula (III). This phenomenon occurs due to the conformation of the first laminate.

Process (4): Optional process

In the method of the present invention, the following steps may be conducted if necessary.

A step of linking the porphyrin residue at the terminal end of the fixed first laminate with one of the porphyrin residues of another meso-meso linked bis-porphyrin represented by the formula (III), via two coordinate bonds, in the same manner as in above (2), thereby obtaining a second laminate represented by the above formula (IV) or (IV'), wherein p represents an integer of 2 or more); and

a step of effecting, in the presence of a Grubbs catalyst, a ring-closing metathesis reaction in the same manner as in above (3), thereby obtaining a fixed second laminate represented by the formula (V) or (V'), wherein p represents an integer of 2 or more);

wherein the linking and the effecting the ring-closing metathesis reaction, as a cycle, are sequentially repeated q times, thereby obtaining a fixed qth laminate represented by the formula (V) or (V'), wherein p represents q, and q is an integer of 2 or more;

By adjusting the number of repeating the process

(4), the number of laminated layers of the photo-
functional molecule element of the present invention
can be set at a desired value. The number of the
molecules which are laminated at one implementation of
5   the process (4) varies depending on the concentration
of the porphyrin solution, time during which the
substrate is soaked, reaction temperature and the like.
For example, in the condition of example described
below, it is assumed that the value of p increases by 2
10   to 3 at each implementation of the process (4).

Further, by changing the type of the meso-meso
linked bis-porphyrin represented by the formula (III),
which is used in the process (4), a gradient-functional
material having a gradient of potential as shown in
15   the schematic view described above can be prepared.

Process (5): a step of linking the porphyrin
residue at the terminal end of the fixed first laminate
obtained in above (3) or the fixed q^{th} laminate
obtained in above (4), with the porphyrin residue of
20   a porphyrin derivative represented by the following
formula (VI):

(VI)

(wherein each of Z_1, M, X, Y, m, n, a, b and d is as

defined above, and Z_2 represents a group having a

functional group which can be an electron acceptor or

electron donor, or a group which can be the terminal

group of the porphyrin polymer), via two coordinate

bonds, thereby obtaining a photo-functional molecule

precursor represented by the following formula (VII) or

(VII'):

(VII)

Substrate

(VII')

Substrate

(wherein each of the substituents is as defined above).

In the process (5), a photo-functional molecule precursor is obtained by soaking (generally for 1 to 5 hours) the fixed first laminate or the fixed q^{th} laminate obtained by the optional process (4) in a solution of a porphyrin derivative having en electron accepting group or electron donating group and represented by the aforementioned formula (VI).
The solvent that may be used is the same as described above in process 2.

Process (6): A step of effecting, in the presence of a Grubbs catalyst, a ring-closing metathesis reaction of the olefin portion derived from the porphyrin derivative represented by the formula (VI), with the olefin portion of the porphyrin residue that is coordinated to the porphyrin derivative, so that the porphyrins are fixed to each other by covalent bonds, thereby obtaining a photo-functional molecule element represented by the following formula (VIII) or (VIII'):
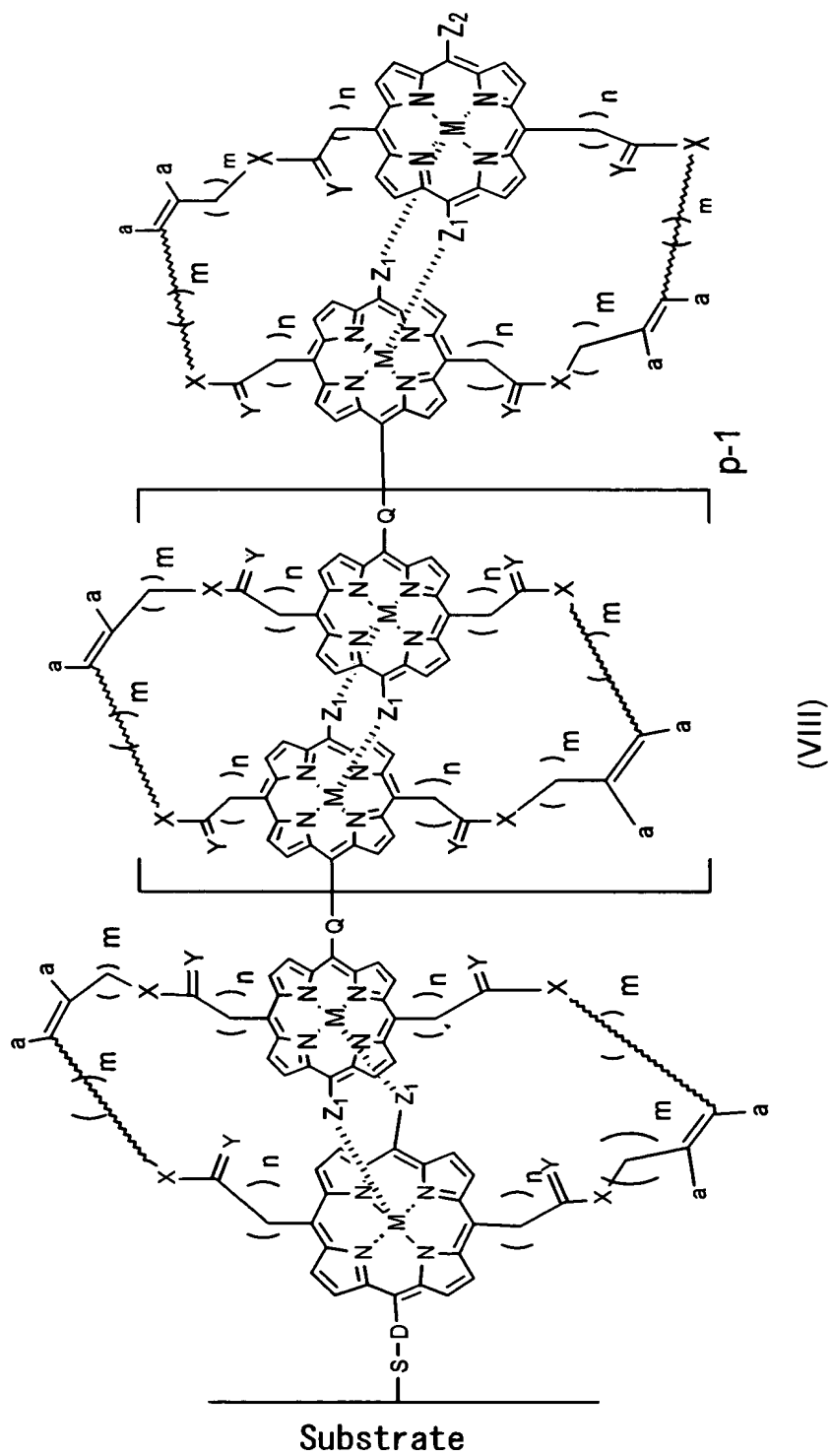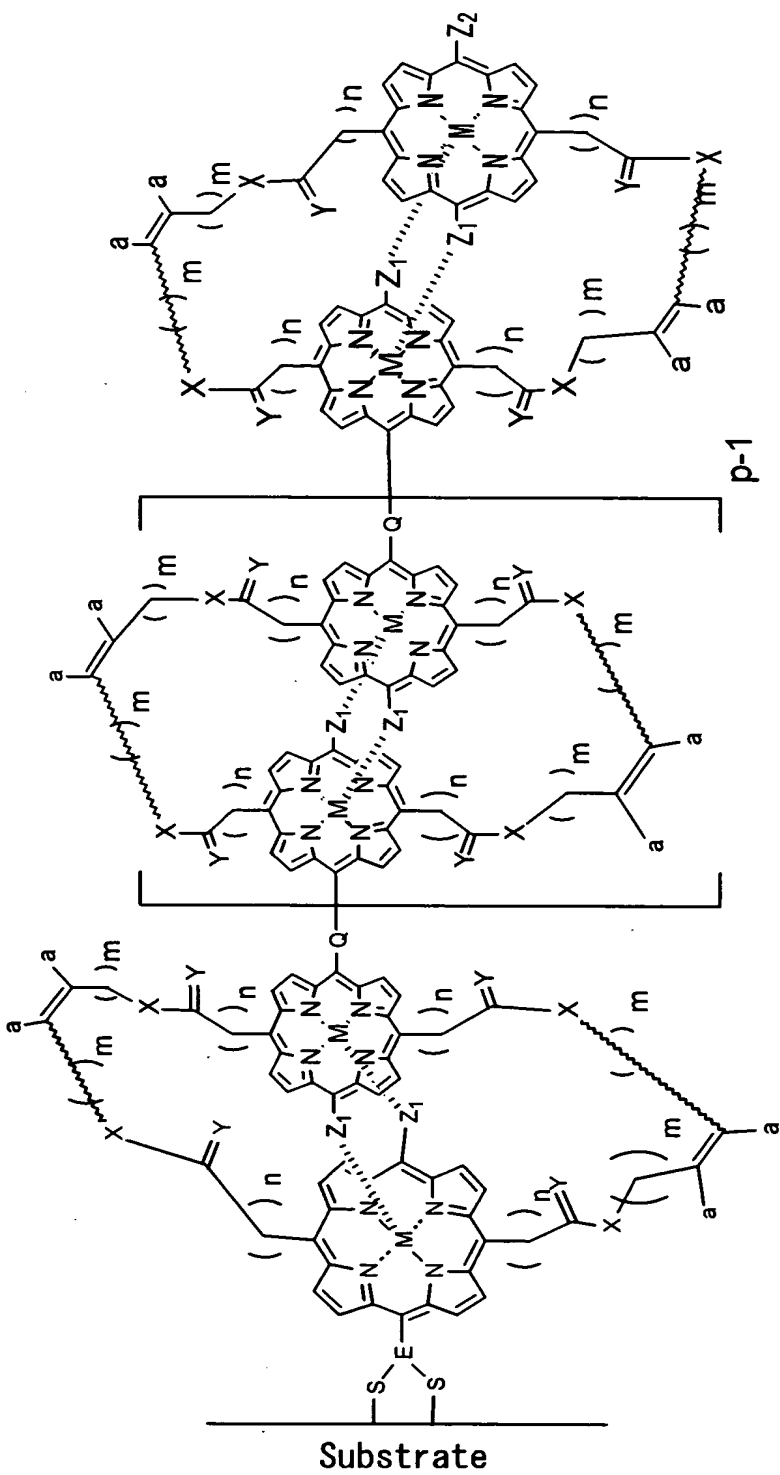
(VIII)

(VIII')

(wherein each of the substituents is as defined above).

The ring-closing metathesis reaction of the process (6) can be carried out in a condition similar to that in the ring-closing metathesis reaction of the process (3).

Examples

Examples of the present invention will be described hereinafter, however, the present invention is not restricted to these examples.

<Example 1>

(1-1) Synthesis of porphyrin molecule

(1-1-1) General operation

The synthesized compounds were identified by the method described below. Silica gel 60 (Merck) was used as a carrier of the column chromatography used for separation of the products. Silica gel 60F254 (Merck) was used as a carrier of the thin layer chromatography (TLC). For detecting a spot, coloring of iodine, 10 % ethanol solution of phosphomolybdic acid and UV luminescence (short 254 nm, long 365 nm) were used in combination. NMR spectrum was measured by dissolving a sample in $CDCl_3$ or $DMSO-d_6$ and using JEOL JNM EX 270 spectrometer (270 MHz) or JEOL ECP 600 spectrometer (600 MHz) as an analyzer, in which measurement tetramethylsilane (TMS) was employed as the internal standard substance. The infrared (IR) absorption spectrum was measured according to the KBr tablet

method by using Nicolet AVATAR 320ES. The UV-visible (UV-VIS) spectrum was measured by using Shimazu UV-3100PC, in which measurement a quartz cell having optical path length of 10 mm or 1 mm was used.

5   The fluorescence spectrum was measured by using Hitachi F-4500. The mass spectrometry was carried out according to the matrix assisted laser desorption ionisation time-of-flight mass spectrometry (MALDI-TOF MS). The mass spectrometry was measured by using

10   PerSeptive Biosystems VoyagerDE-STR as an analyzer. The measurements were conducted with a sample coated on a gold plate together with Dithranol (Aldrich Co., Ltd.) as matrix.

(1-1-2) Compound A-5 was obtained as a result of

15   a reaction shown in the following scheme A:

Scheme A
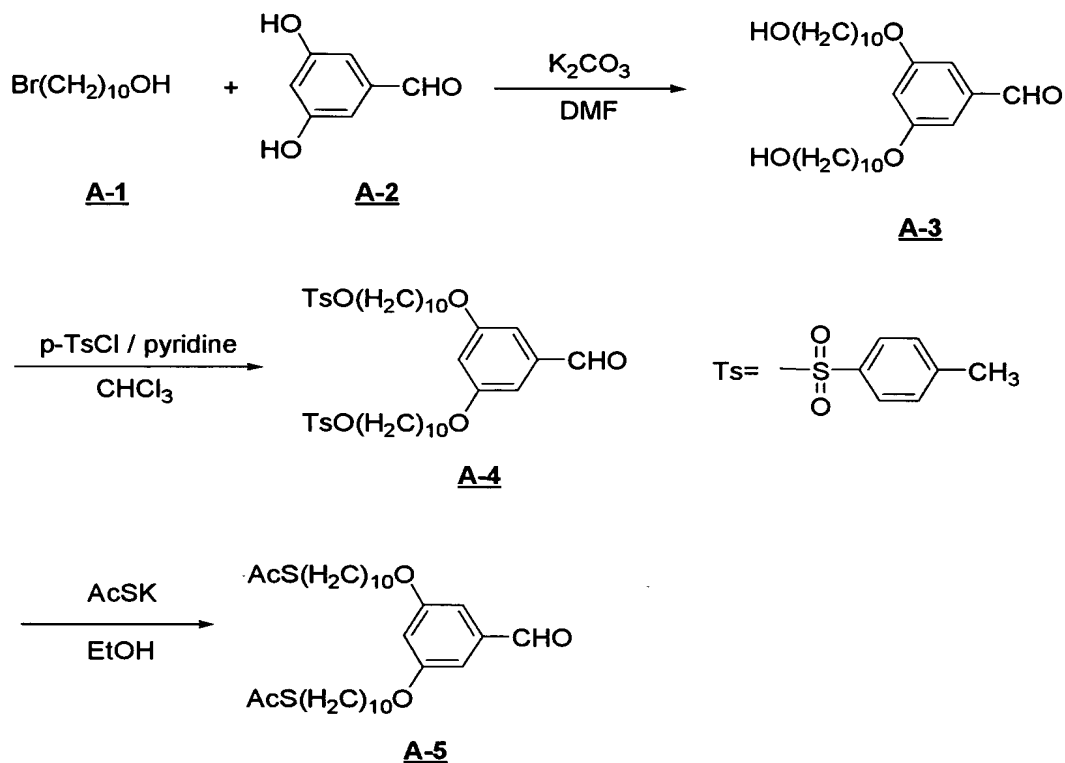
3,5-Bis(10-hydroxydecyloxyl)benzaldehyde A-3

1.18 g of 3,5-dihydroxybenzaldehyde A-2
(8.56 mmol) and 6.15 g of K_2CO_3 (44.5 mmol, 5.2 eq.)
were added to 4.47 g of 10-bromodecane-1-ol A-1
(18.8 mmol, 2.2 eq.) dissolved in 100 mL of DMF, and
the mixture was stirred in nitrogen atmosphere at 50°C
for 48 hours. After the temperature was returned to
room temperature, the reaction was stopped by adding
50 mL of water and the organic layer was extracted with
ether (100 mL × 3). The extracted organic layers were
combined, washed with saturated brine and dried with
anhydrous Na_2SO_4. The solvent was removed by using
an evaporator, whereby brown liquid A-3 was obtained

(crude yield: 4.418 g). The product was not purified
at this stage and directly used for the next reaction.
TLC R_f = 0.63 (eluting solvent : CHCl3/MeOH = 10/1,
detection : UV 254 nm, 10 % ethanol solution of
phosphomolybdic acid)

^{1}H-NMR (270 MHz, CDCl3) δ 9.88 (s, 1H; H_a), 6.98 (d,
J = 6.0 Hz, 2H; H_b), 6.70 (t, J = 6.0 Hz, 1H; H_c), 3.98
(t, 4H; H_d), 3.62 (t, J = 16.8 Hz, 4H; H_e), 1.85-1.26
(m, H_f).

The integrals of He and Hf do not accord, because
the material, 10-bromodecane-1-ol, remained.

$$\underset{a}{OHC}-\overset{\overset{\displaystyle OCH_2(CH_2)_8CH_2OH}{\underset{b}{|}}}{\underset{\underset{d \quad f \quad e}{OCH_2(CH_2)_8CH_2OH}}{\langle\!\!\!\bigcirc\!\!\!\rangle}}c$$
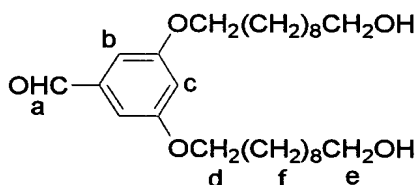
3,5-Bis[10-(p-
toluenesulfonyloxyl)decyloxyl]benzaldehyde A-4

2 g of unpurified A-3 (4.44 mmol) was dissolved in
50 mL of chloroform, and 3.38 g of p-TsCl (17.8 mmol,
4 eq.) and 1.40 g of pyridine (17.8 mmol, 4 eq.) were
added thereto. The solution was stirred at 0°C and
the reaction was allowed to proceed for 9 hours.
The reacted solution was washed with water (50 mL x 3)
and NaHCO3, and then dried with anhydrous Na2SO4
containing a small amount of Na2CO3. The solvent was
removed by using an evaporator, whereby orange color
liquid was obtained. This gross product was separated

by using a silica gel column (CHCl₃/hexane = 3/2), whereby pale yellow, oily A-4 was obtained. Yield was 2.20 g (65 %).

TLC R_f = 0.34 (eluting solvent : hexane/EtOAc = 3/1, detection : UV 254 nm, 10 % ethanol solution of phosphomolybdic acid)

^{1}H-NMR (270 MHz, CDCl₃) δ 9.89 (s, 1H; H_a), 7.79 (d, J = 8.4 Hz, 2H; H_b), 7.34 (d, J = 8.1 Hz, 2H; H_c), 6.98 (d, J = 2.2 Hz , 2H; H_d), 6,69 (t, J = 2.4 Hz, 1H; H_e), 4.04-3.96 (m, 8H; H_f), 6,69 (s, 6H; H_g), 1.81-1.25 (m, 32H; H_h)
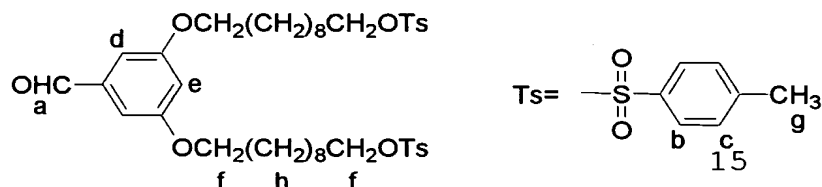
3,5-Bis(10-thioacetyldecyloxyl)benzaldehyde A-5

800 mg of 3,5-Bis[10-(p-toluenesulfonyloxyl) decyloxyl]benzaldehyde A-4 (1.05 mmol) was dissolved in 40 mL of ethanol. 361 mg of potassium thioacetate (3.16 mmol, 3 eq) was added thereto and the mixture was stirred for 2 hours, with reflux. After the temperature of the reacted solution was returned to room temperature, 20 mL of water was added to the solution, and extracted with diethyl ether (50 mL × 3). The extracted ether layers were combined, washed with saturated brine and dried with anhydrous Na₂SO₄.

The solvent was removed by using an evaporator, whereby solid A-5 of beige color was obtained. Yield 447 mg (75 %).

TLC R_f = 0.72 (eluting solvent: hexane/EtOAc = 3/1, detection: UV 254 nm, 10 % ethanol solution of phosphomolybdic acid)

^{1}H-NMR (270 MHz, CDCl$_3$) δ 9.887 (s, 1H; H_a), 7.263 (d, 2H; H_b), 6.981 (t, 2H; H_c), 3.982 (t, J = 6.75 Hz, 4H; H_d), 2.863 (t, J = 7.02 Hz, 4H; H_e), 2.321 (s, 6H; H_f), 1.812-1.305 (m, 32H; H_g)
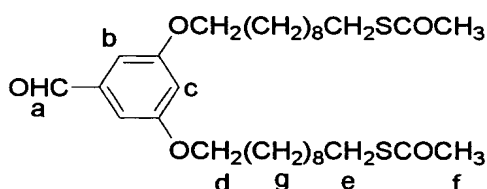
(1-1-3) Compound B-3 was obtained as a result of a reaction shown in the following scheme B:

Scheme B
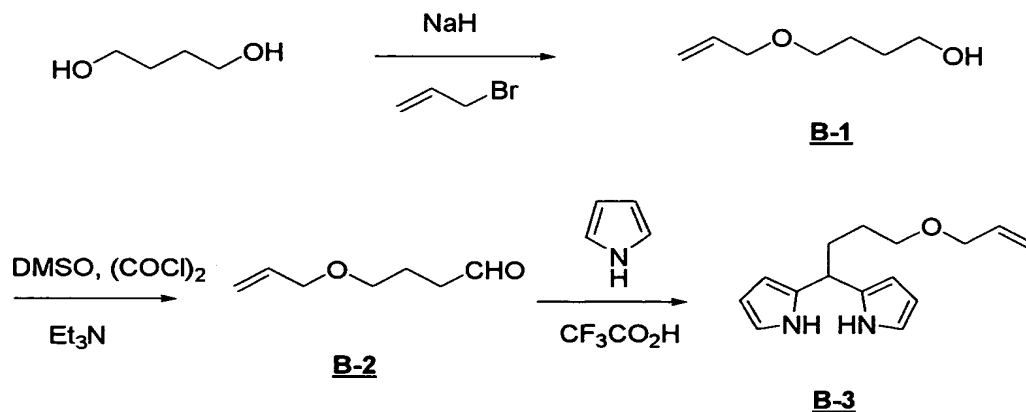
4-Allyloxy-1-butanol B-1 (ref. Kodama, I.; Kawada, M.; Gevorgyan, V.; Yamamoto, Y., J. Org. Chem. 1997, 62, 7439)

1.5 g of sodium hydride (61 mmol) was washed with n-hexane and dispersed to 30 mL of THF. The solution was stirred in an ice bath for 1 hour, while 22 g of butanediol (249 mmol) was added dropwise thereto.

5   7.6 g of allyl bromide (63 mmol) was also added dropwise to the mixture and the mixture was stirred in an ice bath for 1 hour. Thereafter, the reaction solution was heated for 3 hours with reflux (sodium bromide of beige color was deposited). The reaction

10   was quenched by adding water to the solution and the oily phase was separated. Then, the aqueous phase was extracted with Et_2O. The aqueous phase was combined with the previously extracted oily phase and the mixed phases were dried with anhydrous Na_2SO_4. The solvent

15   was distilled away under reduced pressure. The product was purified by distillation under reduced pressure (79 to 82°C/0.3 kPa), whereby colorless, transparent liquid was obtained (6.8 g, 82 %).

^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.64-1.72 (m, $-(CH_2)_2-$, 4H),

20   2.68 (br, $-OH$, 1H), 3.48 (t, J = 6.0 Hz, $-OCH_2-$, 2H), 3.64 (t, J = 6.0 Hz, $-CH_2OH$, 2H), 3.99 (dd, J = 5.9, 1.4 Hz, $CH_2=CHCH_2O-$, 2H), 5.20 (d, J = 10.5 Hz, β-cis-allyl, 1H), 5.37 (dd, J = 17.3, 1.6 Hz, β-trans-allyl, 1H), 5.91 (m, α-allyl, 1H)

25

4-Allyloxy-1-butanal B-2

13 mL of DMSO (246 mmol) was gradually added to

a solution prepared by dissolving oxaryl chloride
(5.8 mL, 66 mmol) in 123 mL of $CHCl_3$, which solution
had been cooled to -80°C, and the mixture was stirred
for three minutes.   6.8 g of 4-allyloxy-1-butanol
(52 mmol) was then added to the mixture. After
the solution was stirred for 15 minutes, 43 mL of
triethylamine (594 mmol) was added thereto and the
reaction solution was stirred for 10 hours, while the
temperature of the reaction solution was allowed to
return to room temperature. The reaction was quenched
by adding distilled water and the $CHCl_3$ layer was
separated. The separated layer was washed with diluted
hydrochloric acid, saturated aqueous sodium bicarbonate
and saturated brine and dried with anhydrous Na_2SO_4.
The solvent was distilled away under reduced pressure,
whereby pale yellow liquid was obtained (6.0 g, 90 %).
^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.93 (m, $-CH_2C\underline{H}_2CH_2-$, 2H),
2.54 (m, $-C\underline{H}_2CHO$, 2H), 3.47 (t, J = 5.9 Hz, allyl-$OC\underline{H}_2-$
, 2H), 3.99 (ddd, J = 5.1, 1.4, 1.4 Hz, $CH_2=CHC\underline{H}_2O-$,
2H), 5.17 (dd, J = 10.5, 1.9 Hz, β-cis-allyl, 1H),
5.25 (dd, J = 15.4, 1.6 Hz, β-trans-allyl, 1H), 5.91
(m, α-allyl, 1H), 9.78 (s, $-C\underline{H}O$, 1H).
bp.45-48°C/0.3 kPa

Meso-(3-Allyloxypropyl)dipyrromethane B-3

       6.0 g of 4-allyl-1-butanal (47 mmol) was dissolved
in 60 equivalent amount of pyrrole (200 mL), and

nitrogen gas was bubbled therein. 0.362 mL, 0.1 equivalent amount, of TFA (4.7 mmol) was added thereto, and stirred for 14 hours (during which the solution became dark), and $CHCl_3$ was added, then subjected to liquid separation washing using saturated aqueous sodium bicarbonate and saturated brine, and dried with anhydrous Na_2SO_4. The solvent was distilled away under reduced pressure, and excess pyrrole was recovered by distillation under reduced pressure. The desired product (9.3 g) of brownish viscous liquid was obtained using silica gel column (hexane/ethyl acetate 5/1 v/v, TLC R_f = 0.28) (yield 81 %).

^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.58 (m, $-CH_2\underline{CH_2}CH_2-$, 2H), 2.04 (m, $-CH_2\underline{CH_2}$-dipyrro, 2H), 3.43 (t, J = 6.2 Hz, allyl-$OC\underline{H}_2-$, 2H), 3.93 (t, J = 1.4 Hz, $CH_2=CHC\underline{H}_2O-$, 2H), 4.02 (t, methine, 1H), 5.16 (d, J = 10.5 Hz, β-cis-allyl, 1H), 5.25 (dd, J = 17.1, 1.4 Hz, β-trans-allyl, 1H), 5.89 (m, α-allyl, 1H), 6.05 (s, 3,3'-pyrrole ring, 2H), 6.14 (m, 4,4'-pyrrole ring, 2H), 6.62 (s, 5,5'-pyrrole ring, 2H), 7.88 (br, N$\underline{H}$, 2H)

(1-1-4) Compound C-3 was obtained by the reaction of the following scheme C:

Scheme C
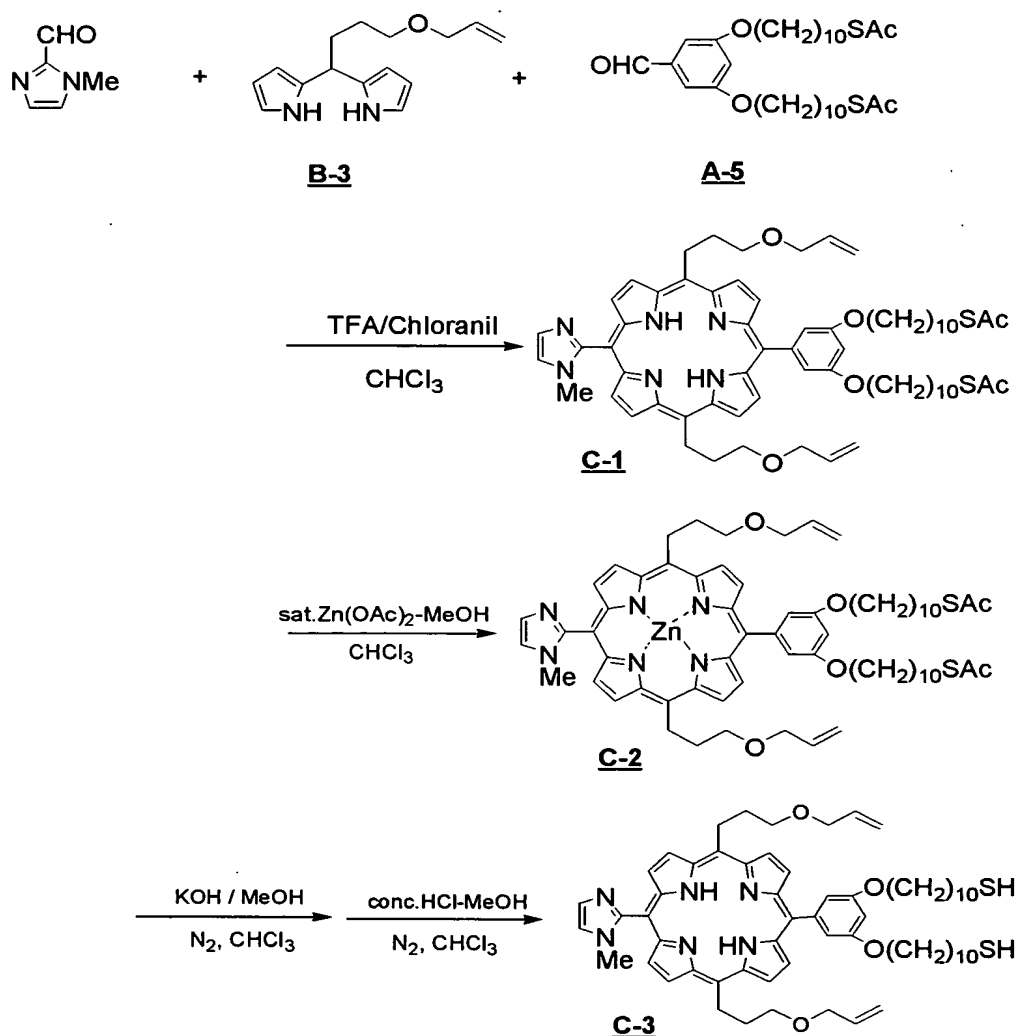
5,15-Bis(allyloxypropyl)-10-[3,5-bis(10-
thioacetyldecyloxyl)phenyl]-20-(1-methyl-2-imidazol)
porphyrin C-1

612 mg of meso-(allyloxypropyl)dipyrromethane B-3
(2.59 mmol, 2 eq.) and 733 mg of 3,5-bis(10-
thioacetyldecyloxyl)-benzaldehyde A-5 (1.29 mmol, 1eq.)
were added to a solution of 142 mg of 2-Formyl-1-
methylimidazole (1.29 mmol, 1 eq.) dissolved in 250 mL

of $CHCl_3$, and nitrogen gas was bubbled thereinto for 10 min. To the solution, 199 μL of trifluoroacetic acid (2.59 mmol, 2 eq.) was added as a acid catalyst, and stirred for 5 hours under nitrogen atmosphere with light shielding. 954 mg of p-chloranil (3.88 mmol, 3 eq.) was further added as an oxidizer, and stirred the mixture overnight to finish the reaction. The reaction solution was passed through silica gel as it is, and the tar component and by-products were removed by column chromatography (eluting solvent $CHCl_3$ → $CHCl_3$/acetone = 9/1, v/v). The fraction showing R_f = 0.40 in TLC (eluting solvent:$CHCl_3$ / acetone = 9/1,v/v) was separated by silica gel column chromatography (eluting solvent $CHCl_3$ / acetone = 9/1 →$CHCl_3$ / acetone = 1/1, v/v) again, to separate C-1 (59.6 mg, yield 4.1 %).

TLC R_f = 0.40 (eluting solvent: $CHCl_3$/acetone = 9/1, Detection: UV 365 nm, visible)

^{1}H-NMR (600 MHz, $CDCl_3$) δ 9.53 (d, J = 4.8 Hz, 2H; Por β), 9.47 (d, J = 4.8 Hz, 2H; Por β), 9.00 (d, J = 4.8 Hz, 2H; Por β), 8.77 (d, J = 4.8 Hz, 2H; Por β), 7.69 (s, 1H; imidazole ring), 7.48 (s, 1H; imidazole ring), 7.39 (s, 1H; phenyl), 7.30 (s, 1H; phenyl), 6.91 (s, 1H; phenyl), 6.08 (ddt, J = 6.0, 9.6, 16.2 Hz, 2H; Allyl β), 5.42 (dd, J = 1.8, 16.2 Hz, 2H; Allyl γ), 5.23 (dd, J = 1.8, 9.6 Hz, 2H; Allyl γ), 5.10 (t, J = 7.2 Hz, 4H; $CH_2 \alpha$), 4.12 (m, 4H; $phOCH_2$-), 4.08 (m, 4H;

Allylα), 3.66 (t, , J = 4.8 Hz 4H; -C$\underline{H}_2$OAllyl), 3.40

(s, 3H; NCH_3), 2.83 (m, 4H; -C$\underline{H}_2$SAc), 2.79 (m, 4H; CH$_2$

β), 2.28 (s, 6H; -SCOC$\underline{H}_3$), 1.88-1.25 (m, 32H; Alkyl),

-2.65 (s, 2H; inner proton).

5   MALDI-TOF Mass spectrum (Dithranol): m/z Found 1123.96

(M+H)+, Calcd ($C_{66}H_{86}N_6O_6S_2$) 1122.61

UV-Vis spectrum (solvent: CHCl$_3$) λ_{max}/nm (absorbance):

419.0(0.1109), 516.0 (0.0075), 554.5(0.0030)

588.5(0.0028), 649.0(0.0020)

10   Fluorescence spectrum (solvent: CHCl$_3$, λ_{EX}: 419 nm)

λ_{EM}/nm (fluorescent intensity): 653(211.0),

719.8(102.1).

5,15-Bis(allyloxypropyl)-10-[3,5-bis(10-

15   thioacetyldecyloxyl)phenyl]-20-(1-methyl-2-imidazolyl)

porphyrinatozinc C-2

      28 mg of C-1 (24.9 μmol) was dissolve into 6 mL

of CHCl$_3$ under nitrogen atmosphere, and 1 mL of

methanol solution of saturated zinc acetate was added,

20   then stirred for 2 hours. The reaction was stopped

after observing, in TLC (eluting solvent: CHCl3/acetone

= 9/1,v/v), the disappearance of C-1 and instead

appearance of C-2 at R$_f$ = 0.80. 5 mL of CHCl$_3$ was

added to the reaction solution, and washed with an

25   aqueous solution of saturated sodium bicarbonate and

purified water, then extracted with CHCl$_3$ until the

water layer became colorless. The organic layer was

combined, and washed with saturated brine, and dried with anhydrous sodium sulfate. The solvent was concentrated with evaporator, and C-2 was separated by silica gel column chromatography (eluting solvent: $CHCl_3$/acetone = 9/1,v/v) (26.6 mg, yield 90 %).

TLC R_f = 0.80 (eluting solvent: : $CHCl_3$/acetone = 9/1, detection: : UV 365 nm, visible)

^{1}H-NMR (600 MHz, $CDCl_3$) δ 9.62 (d, J = 4.8 Hz, 2H; Por β), 9.51 (d, J = 4.8 Hz, 2H; Por β), 8.95 (d, J = 4.8 Hz, 2H; Por β), 7.87 (s, 1H; phenyl), 7.31 (s, 1H; phenyl), 6.98 (s, 1H; phenyl), 6.19 (ddt, J = 6.0, 10.2, 16.8 Hz, 2H; Allyl β), 5.53 (dd, J = 1.2, 16.8 Hz, 2H, Allyl γ), 5.52 (d, J = 1.8 Hz, 1H; imidazole ring), 5.41 (d, J = 4.8 Hz, 2H; Por β), 5.34 (dd, J = 1.2, 10.2 Hz, 2H; Allyl γ), 5.23 (m, 4H; $CH_2 \alpha$), 4.37 (t, J = 7.2 Hz, 2H; PhO$\underline{CH_2}$-), 4.08 (ddt, J = 1.2, 6.0, 10.2 Hz, 4H; Allyl α), 4.12 (t, J = 6.6 Hz, 2H; PhO$\underline{CH_2}$-), 3.94 (m, 4H; -$\underline{CH_2}$OAllyl), 3.11 (m, 2H; CH_2 β), 3.00 (m, 2H; CH_2 β), 2.83 (t, J = 7.2 Hz, 2H; -$\underline{CH_2}$SAc), 2.83 (t, J = 7.2 Hz, 2H; -$\underline{CH_2}$Sac), 2.32 (s, 3H; -SCO$\underline{CH_3}$), 2.27 (s, 3H; -SCO$\underline{CH_3}$), 2.12 (d, J = 1.8 Hz, 1H; imidazole ring), 1.67 (s, 3H; NCH_3), 2.06-1.26 (m, 32H; Alkyl).

MALDI-TOF Mass spectrum (Dithranol) : m/z Found 1185.89 (M+H)$^+$, Calcd ($C_{66}H_{84}N_6O_6S_2Zn$) 1184.52

UV-Vis spectrum (solvent: $CHCl_3$) λ_{max}/nm (absorbance): 414.0(0.0851), 437.0(0.0991), 566.0(0.0082),

618.5(0.0045)

Fluorescent spectrum (solvent: $CHCl_3$, λ_{EX} : 437 nm)

λ_{EM}/nm (fluorescent intensity): 622.8(167.5),

678.2(55.27)

5,15-Bis(allyloxypropyl)-10-[3,5-bis(10-

mercaptodecyloxyl)phenyl]-20-

(1-methyl-2-imidazolyl) porphyrin C-3

26.6 mg of C-2 (22.4 μmol) was dissolved into

10 mL of a mixed solution of $CHCl_3$ / MeOH (= 4/1, v/v),

and N_2 was bubbled for 5 min. 1 mL of KOH solution

(KOH 5 g + H_2O 10 mL + MeOH 15 mL) was added thereto

and stirred at room temperature for 30 min. After

confirming the disappearance of C-2 by MALDI-TOF Mass

spectrum, purified water was added to stop the

reaction. The mixture was washed with purified water

twice, and extracted with $CHCl_3$ until the water layer

became colorless.

The organic layer was combined, and conc. HCl /

MeOH (= 1 / 10, v/v) was added until the color of the

solution changed to fresh green, and stirred at room

temperature for 2 hours. The generation of the desired

product was confirmed by MALDI-TOF Mass spectrum and

TLC ($CHCl_3$ / acetone = 9 / 1) with R_f=0.40. The

reaction solution was washed with an aqueous solution

of saturated sodium bicarbonate (50 mL) and purified

water (50 mL), and the water layer was extracted with

CHCl$_3$, and then dried with anhydrous Na$_2$SO$_4$. The solvent was removed by evaporator, and C-3 was obtained after suction drying (20.3 mg, yield 87 %).

TLC R$_f$ = 0.40 (eluting solvent: : CHCl$_3$/acetone = 9/1, detection: : UV 365 nm, visible)

^{1}H-NMR (600 MHz, CDCl$_3$) δ 9.45 (d, J = 4.2 Hz, 2H; Por β), 9.39 (d, J = 4.2 Hz, 2H; Por β), 8.92 (d, J = 4.2 Hz, 2H; Por β), 8.70 (d, J = 4.2 Hz, 2H; Por β), 7.61 (s, 1H; imidazole ring), 7.39 (s, 1H; imidazole ring), 7.32 (s, 1H; phenyl), 7.22 (s, 1H; phenyl), 6.83 (s, 1H; phenyl), 6.00 (ddt, J = 6.0, 9.6, 16.2 Hz 2H; Allyl β), 5.34 (dd, J = 1.8, 18.0 Hz, 2H; Allyl γ), 5.18 (dd, J = 1.8, 10.2 Hz, 2H; Allyl γ), 5.11 (t, J = 7.80 Hz 4H; CH$_2$ α), 4.06 (m, 4H; phOC$\underline{H}_2$-), 4.00 (m, 4H; Allyl α), 3.58 (t, J = 6.0 Hz 4H; -C$\underline{H}_2$OAllyl), 3.31 (s, 3H; NCH$_3$), 2.71 (m, 4H; CH$_2$ β), 2.40 (m, 4H; -C$\underline{H}_2$SH), 1.81-0.77 (m, 32H; Alkyl), -2.77 (s, 2H; inner proton).

MALDI-TOF Mass spectrum (Dithranol) : m/z Found 1039.68 (M+H)$^+$, Calcd (C$_{62}$H$_{82}$N$_6$O$_4$S$_2$) 1038.58

UV-Vis spectrum(solvent: CHCl$_3$) λ_{max}/nm (absorbance): 418.5(0.1128), 515.5 (0.0059), 553.5(0.0024) 589.5(0.0022), 648.0(0.0018)

Fluorescent spectrum (solution: CHCl$_3$, λ_{EX} : 419 nm) λ_{EM}/nm (fluorescent intensity): 653(177.3), 718.6(84.28)

(1-1-5) Compound D-3 was obtained by the reaction of the following scheme D:

Scheme D

B-3

D-1

D-2

D-3
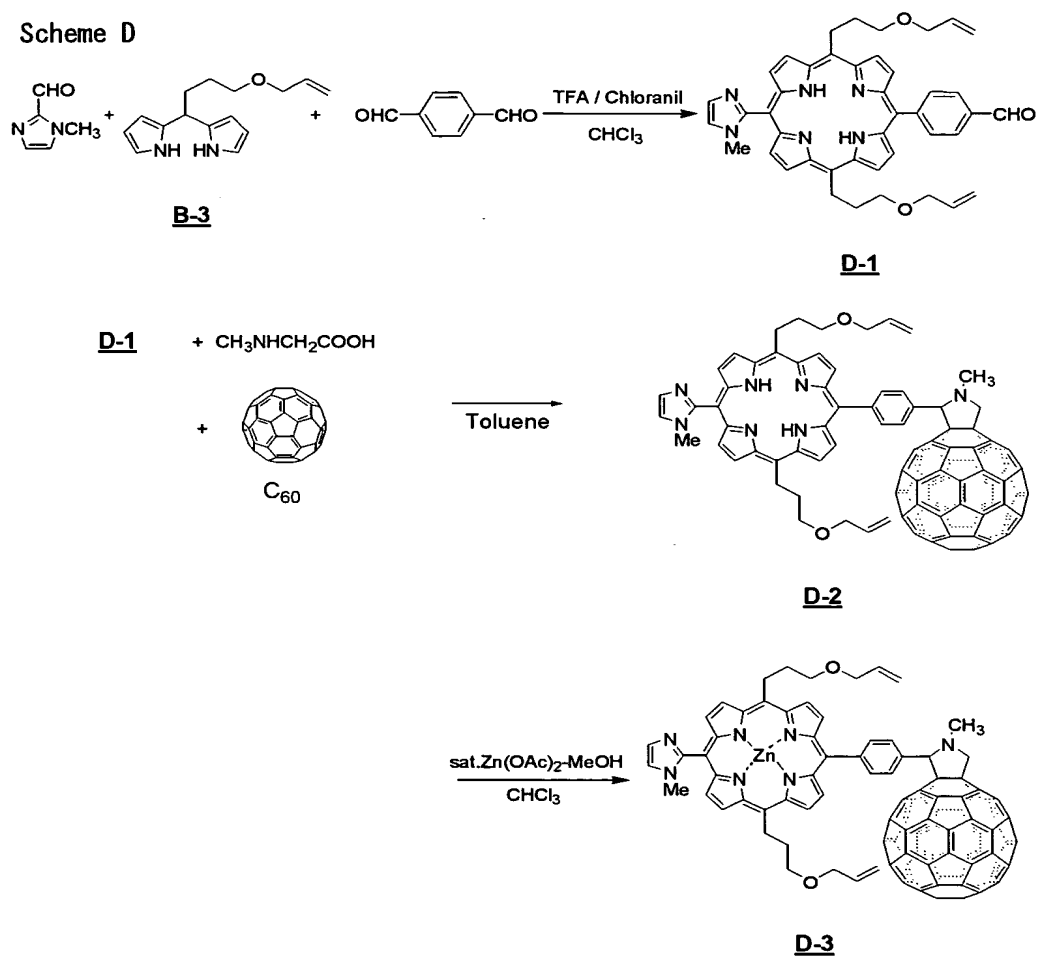
5,15-Bis(allyloxypropyl)-10-(4-formylphenyl)-20-(1-
methyl-2-imidazolyl) porphyrin D-1

5   1.00 g of 5-(allyloxypropyl)dipyrromethane B-3
(4.09 mmol, 2 eq.) and 274 mg of terephthalaldehyde
(2.05 mmol, 1eq.) were added to 225 mg of 2-Formyl-1-
methylimidazole (2.05 mmol, 1 eq.) dissolved in 400 mL
of CHCl3, and nitrogen gas was bubbled for 10 min.

10   To the solution, 315 μL of trifluoroacetic acid
(4.09 mmol, 2 eq.) was added as an acid catalyst, and
stirred for 30 min under nitrogen atmosphere with light
shielding. 1.51 g of chloranil (6.14 mmol, 3 eq.) was

further added as an oxidizer, and stirred the mixture overnight to finish the reaction. The tar in the reaction solution was removed by suction filtration, and the residue was washed with $CHCl_3$. The filtrate

5 was washed with 200 mL of an aqueous solution of saturated sodium bicarbonate, and 200 mL of purified water. The water layer was extracted with $CHCl_3$, and dried with anhydrous Na_2SO_4. The tar component and by-products were removed with silica gel column

10 chromatography (eluting solvent: $CHCl_3$ → $CHCl_3$ / MeOH = 9/1, v/v). The fraction showing R_f = 0.48 in TLC (eluting solvent: :$CHCl_3$/acetone = 1/1,v/v) was separated again by silica gel column chromatograph (eluting solvent: $CHCl_3$/acetone = 1/1, v/v) again, to

15 obtain D-1(65.3 mg, yield 4.6 %).

TLC R_f = 0.48 (eluting solvent: $CHCl_3$/acetone = 1/1, detection: :UV 365 nm, visible)

^{1}H-NMR (600 MHz, $CDCl_3$) δ 10.41 (s, 1H; -CHO), 9.55 (d, J = 4.2 Hz, 2H; Porβ), 9.51 (d, J = 4.2 Hz, 2H; Porβ),

20 8.81 (d, J = 5.4 Hz, 2H; Porβ), 8.80 (d, J = 5.4 Hz, 2H; Porβ), 8.42 (d, J = 7.2 Hz, 1H; phenyl), 8.31 (t, 2H; phenyl), 8.28 (d, J = 7.2 Hz, 1H; phenyl), 7.69 (s, 1H; imidazole ring), 7.49 (s, 1H; imidazole ring), 6.08 (ddt, J = 6.0, 9.6, 16.2 Hz 2H; Allylβ), 5.43 (dd, J =

25 1.2, 17.4 Hz 2H; Allylγ), 5.26 (dd, J = 1.2, 10.2 Hz 2H; Allylγ), 5.01 (t, J = 7.20 Hz 4H; $CH_2\alpha$), 4.08 (m, 4H; Allylα), 3.66 (t, , J = 5.4 Hz 4H; -C$\underline{H}_2$OAllyl),

3.31 (s, 3H; NCH$_3$), 2.28 (m, 4H; CH$_2\beta$), -2.69 (s, 2H;

inner proton).

MALDI-TOF Mass spectrum (Dithranol): m/z Found 691.34

(M+H)$^+$, Calcd (C$_{43}$H$_{42}$N$_6$O$_3$) 690.33

UV-Vis spectrum (solvent: CHCl$_3$) λ_{max}/nm (absorbance):

418.0(0.8446), 515.5(0.0455), 551.0(0.0222),

591.0(0.0147), 648.0(0.0120)

Fluorescent spectrum (CHCl$_3$ λ_{EX}: 418 nm) λ_{EM}/nm

(fluorescent intensity): 653.0(158.9), 711.8(64.28).

5,15-Bis(allyloxypropyl)-10-[4-phenyl-2-(N-

methyl)fulleropyrrolidinyl]-20- (1-methyl-2-imidazolyl)

porphyrin D-2

37.5 mg of D-1 (54.2 μmol) was dissolved into

60 mL of toluene, and 78.1 mg of fullerene (109 μmol,

2 eq.) and 96.7 mg of N-methylglycine (sarcosine)

(1.09 mmol, 20 eq.) were added thereto. The mixture

was stirred under nitrogen atmosphere, and heated

at 100℃ for 12 hours with light shielding. After

confirming the disappearance of D-1 and generation

of D-2 by MALDI-TOF Mass spectrum, the reaction was

stopped. The reaction solution was passed through

silica gel column as it is, fullerene was eluted with

only toluene, at first, to recover it. Subsequently,

the eluting solvent was changed to CHCl$_3$/acetone (=

9/1,v/v), and the red band corresponding to R$_f$ = 0.35

in TLC (eluting solvent: : CHCl$_3$/acetone = 9/1,v/v) was

separated to isolate D-2 (32 mg, yield 41 %).

TLC R_f = 0.35 (eluting solvent: :$CHCl_3$/acetone = 9/1,

detection: :UV 365 nm, visible)

MALDI-TOF Mass spectrum (Dithranol): m/z Found 1439.96

$(M+H)^+$, Calcd $(C_{105}H_{47}N_7O_2)$ 1437.38

UV-Vis spectrum(solvent: $CHCl_3$) λ_{max}/nm (absorbance):

419.0(1.0652), 516.0(0.0582), 551.0(0.0277),

591.5(0.0184), 648.5(0.0140)

Fluorescent spectrum $(CHCl_3 \lambda_{EX}$: 419 nm) λ_{EM}/nm

(fluorescent intensity): 655.0(1.521), 711.8(1.507)

5,15-Bis(allyloxypropyl)-10-[4-phenyl-2-(N-

methyl)fulleropyrrolidinyl]-20- (1-methyl-2-imidazolyl)

porphyrinatozinc D-3

7.7 mg of D-2 (5.35 μmol) was dissolved into

15 mL of $CHCl_3$ under nitrogen atmosphere, and 1 mL of

a methanol solution of saturated zinc acetate was

added, then stirred at room temperature for 2 hours.

The reaction was completed after confirming, in TLC

(eluting solvent: $CHCl_3$/acetone = 9/1,v/v),

disappearance of D-2 and generation of D-3 at R_f=0.85.

5 mL of chloroform was added to the reaction solution,

washed with an aqueous solution of saturated sodium

bicarbonate and purified water, and extracted with

chloroform until the water layer became colorless.

The organic layer was combined, and washed with

saturated brine, and then dried with anhydrous Na_2SO_4.

The solvent was concentrated with evaporator, and D-3 was isolated by separation with silica gel column chromatography (eluting solvent: $CHCl_3$/acetone = 9/1,v/v) (7.2 mg, yield 90 %)

TLC R_f = 0.85 (eluting solvent: $CHCl_3$/acetone = 9/1, detection: : UV 365 nm, visible)

MALDI-TOF Mass spectrum (Dithranol): m/z Found 1502.77 $(M+H)^+$, Calcd $(C_{105}H_{45}N_7O_2Zn)$ =1499.29

UV-Vis spectrum (solvent: $CHCl_3$) λ_{max}/nm (absorbance): 414.0(0.0824), 438.5(0.1113), 565.5 (0.0099), 619.5(0.0063)

Fluorescent spectrum ($CHCl_3 \lambda_{EX}$: 438 nm) λ_{EM}/nm (fluorescent intensity): 620.6(0.581), 675.0(0.300)

(1-1-6) Compound E-6 was obtained by the reaction of the following scheme E:

Scheme E
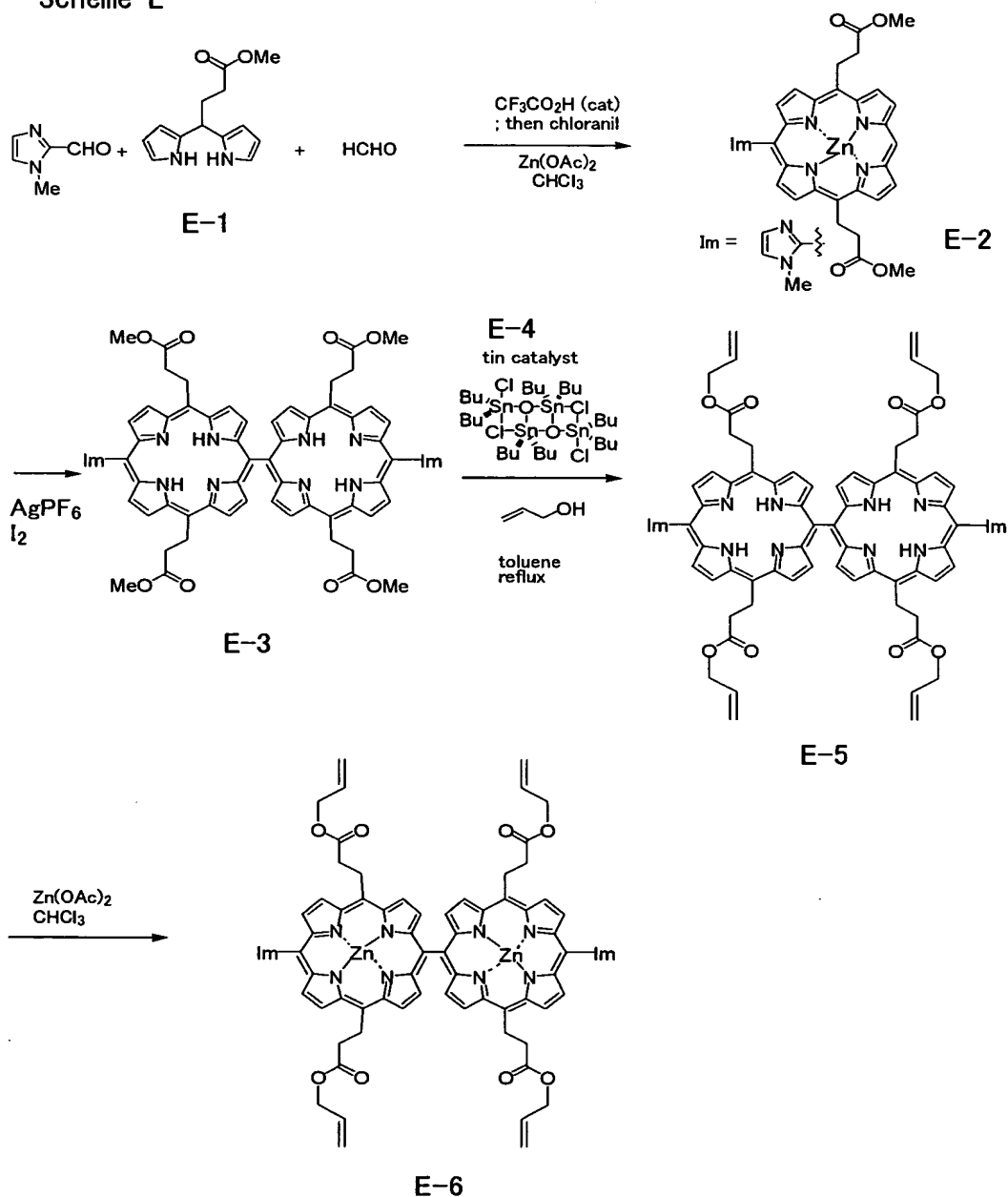
meso-(methoxycarbonylethyl)dipyrromethane E-1

E-1 was synthesized by stirring
methoxycarbonylpropanal (11.6 g, 0.1 mol) and pyrrole
(280 mL, 4 mol) in the presence of trifluoroacetic acid
(1.4 mL, 10 mmol). Purification with silica gel column
chromatography (hexane/EtOAc 5/1) was performed to

obtain 17 g of meso-
(methoxycarbonylethyl)dipyrromethane E-1 (73%).

^{1}H NMR (600 MHz, CDCl$_3$) δ 2.22-2.26 (m, 2H), 2.29-2.33
(m, 2H), 3.63 (s, 3H), 3.99 (t, J = 7.2 Hz, 1H), 6.05-
6.07 (m, 2H, pyH4), 6.12-6.14 (m, 2H, pyH5), 6.58 -
6.62 (m, 2H, pyH2), 7.78 (br, 2H, NH); ^{13}C NMR
(150 MHz, CDCl$_3$) δ 29.5, 31.9, 36.9, 51.6, 105.8,
108.1, 117.3, 132.4, 174.0

5-(1-methylimidazol-2-yl)-10,20-bis(2-
methoxycarbonylethyl)
porphyrin E-2

500 mL of CHCl$_3$ into which 2.6 g of anhydrous
MgSO$_4$ (22 mmol) and 0.8 g of paraformaldehyde (20 mmol)
were dispersed, was bubbled with nitrogen, and
then 0.75 mL of TFA (9.8 mmol) was added. The mixture
was exposed to ultrasound for 40 seconds, 0.55 g
of imidazolylaldehyde (5.0 mmol) and 2.35 g of
dipyromethane E-1 (10 mmol) were added, and the mixture
was stirred for 50 minutes. Then, 3.5 g of chloranil
(14 mmol) was added and stirred for 20 min.
Subsequently, the mixture was subjected to separation
washing with an aqueous solution of saturated sodium
bicarbonate, TFA was removed, and the solvent was
removed under reduced pressure. The fraction
containing the desired porphyrin was separated by
silica gel column chromatography (CHCl$_3$-CHCl$_3$/acetone

9/1 v/v). Zinc was introduced into porphyrin using methanol solution of saturated zinc acetate, and separated with silica gel column (CHCl$_3$). The thus obtained fraction was washed with diethyl ether, and the precipitated fine crystal of E-2 was obtained (96 mg, yield 3.1 %).

^{1}H NMR (270 MHz, CDCl$_3$) δ 1.59 (s, N-CH$_3$, 3H), 1.85 (s, 5-imidazolyl, 1H), 3.87-3.91 (m, -CH$_2$COOMe, 4H), 3.91 (s, -COOCH$_3$, 6H), 5.42 (s, 3,7-β-pyrrole, 2H), 5.44 (s, 4-imidazolyl, 1H), 5.52 (t, J = 8.6 Hz, -CH$_2$CH$_2$COOMe, 4H), 8.95 (d, J = 4.6 Hz, 2, 8-β-pyrrole, 2H), 9.54, 9.74 (d, 4.32 Hz, 12,13, 17,18-β-pyrrole, 4H), 10.29 (s, meso-proton, 1H).

MALDI-TOF Mass spectrum (Dithranol): m/z Found 625.35 (M+H)$^+$, Calcd 624.15 (M$^+$)

UV-Vis spectrum(solvent: CHCl$_3$) λ_{max}/nm (absorbance): 408, 430, 559, 608

15,15'-Bis{5-(1-methylimidazol-2-yl)-10,20-bis(2-methoxycarbonyl-ethyl)}-porphyrin E-3 (meso-meso bisporphyrin)

174 mg of porphyrinato zinc E-2 (0.27 mmol), as a precursor, and 39 mg of I$_2$ (0.15 mmol) were dissolved into 90 mL of CHCl$_3$, and the atmosphere was changed to nitrogen by 5-minute nitrogen bubbling. An acetonitrile solution containing 47 mg of AgPF$_6$ (0.18 mmol) was added drop wise to this solution, and

stirred for 18 minutes at room temperature.

The reaction was quenched by washing the mixture with
an aqueous solution of sodium thiosulfate, aqueous
solution of saturated sodium bicarbonate and saturated
brine, and dried with anhydrous Na_2SO_4, after the
mixture was processed with dilute hydrochloric
acid/methanol solution to remove zinc. After washing
with n-hexane using silica gel column ($CHCl_3$/acetone
9/1 v/v) thrice, the desired porphyrin E-3 in which
porphyrins are directly bonded at meso position was
obtained (74 mmol, yield 49%)

^1H NMR (270 MHz, $CDCl_3$) δ -2.17 (s, NH, 4H), 3.53
(s, N-CH3 + -CH2COOMe, 6H + 8H), 3.70 (d, J = 3.24 Hz,
-COOCH3, 6H), 5.33 (m, -CH2CH2COOMe, 8H), 7.56 (d, J =
1.4 Hz, 5-imidazolyl, 2H), 7.76 (d, J = 1.4 Hz,
4-imidazolyl, 2H), 7.99, 8.14 (d, J = 4.7 Hz,
13,13',17,17'-β-pyrrole, 4H), 8.94 (d, J = 4.1 Hz,
4,4',7,7'-β-pyrrole, 4H), 9.14 (dd, J = 10.8, 5.1 Hz,
12,12',18,18'-β-pyrrole, 4H), 9.59 (dd, J = 2.3,
3.0 Hz, 3,3',9,9'-β-pyrrole, 4H).

MALDI-TOF Mass spectrum (Dithranol):m/z Found 1123.82
$(M+H)^+$, Calcd 1122.45 (M^+).

UV-Vis spectrum(solvent: $CHCl_3$) λmax/nm (absorbance):
413, 453, 526, 596, 655

15,15'-Bis{5-(1-methylimidazol-2-yl)-10,20-bis(2-
allyloxycarbonyl-ethyl)}-porphyrin E-5

21 mg of porphyrin methyl ester E-3 (0.019 mmol) was dissolved into toluene/allyl alcohol 10/1 v/v, and 104 mg, 10 equivalent amount, of tin-catalyst E-4 (0.19 mmol) (prepared by the method of Otera et al., i.e., Junzo Otera, Nobuhisa Dan-oh, Hitosi Nozaki, J. Org. Chem. 1991, 56, 5307-5311) was added and stirred for 6 hours while heating (bath temperature: 80-90℃). After confirming the completion of the transesterification by MALDI-TOF MS, the reaction solution was concentrated with evaporator, purified with silica gel column (CHCl3/acetone 5/1 v/v → 1/1 v/v, CHCl$_3$/acetone 1/1 v/v - CHCl$_3$/acetone 1/1 v/v + MeOH), thereby to obtain E-5 (12 mg, yield 51%).

^{1}H NMR (270 MHz, CDCl3) δ -2.16 (s, NH, 4H), 3.53 (s, N-CH$_3$ + -CH$_2$COOMe, 6H + 8H), 3.50 (m, -CH$_2$COO- 6H), 3.53 (s, N-CH$_3$, 6H), 4.62 (m, -COOCH$_2$-, 8H), 5.15 (d, J =10.26 Hz, β-allyl, 4H), 5.23 (d, J =2.7 Hz, β-allyl, 4H), 5.29 (m, -CH$_2$CH$_2$COO-, 8H), 5.84 (m, α-allyl, 4H), 7.25 (s, 5-imidazolyl, 2H), 7.57 (d, J = 1.1 Hz, 4-imidazolyl, 2H), 7.99, 8.15 (d, J = 4.7 Hz, 13,13',17,17'-β-pyrrole, 4H), 8.95 (d, J = 4.3 Hz, 4,4',7,7'-β-pyrrole, 4H), 9.18 (dd, J = 13.5, 4.9 Hz, 12,12',18,18'-β-pyrrole, 4H), 9.59 (dd, J = 2.3, 3.0 Hz, 3,3',9,9'-β-pyrrole, 4H).

MALDI-TOF Mass spectrum (Dithranol): m/z Found 1227.58 (M+H)$^+$, Calcd 1226.51 (M$^+$)

15,15'-Bis{5-(1-methylimidazol-2-yl)-10,20-bis(2-allyloxycarbonyl-ethyl)}-porphyrinatezinc E-6

The free base porphyrin E-5 (12 mg) was dissolved into chloroform (20 mL), and stirred for 2 hours at room temperature after adding methanol solution of saturated zinc acetate (2 mL). After the reaction liquid was subjected to separation washing with aqueous ethylenediaminetetraacetic acid and saturated brine, the liquid was dried with anhydrous sodium sulfate, thereby zinc complex E-6 (12 mg) was obtained after removing the solvent.

MALDI-TOF Mass spectrum (Dithranol):m/z Found 1351.35 $(M+H)^+$, Calcd 1350.34 (M^+).

UV-Vis spectrum(solvent: CH_2Cl_2) λ max/nm (absorbance): 407, 490, 582, 633.

Fluorescent spectrum (CH_2Cl_2 λ_{EX}:490 nm) λ_{EM}/nm (fluorescent intensity): 670

(1-2) Preparation of porphyrin-organized substrate

(1-2-1) Preparation of gold substrate

Slide glass (76×26×1.2 mm, produced by Iwaki) was soaked into a mixed solution of 30% H_2O_2/conc.HCl (10/1, v/v) for 1.5 to 2 hours. Then, the glass was washed with purified water, and dried with heat gun. The substrate was put into a vapor deposition apparatus, and vapor deposition was performed, firstly, by Cr with 50 Å (vapor deposition rate: ca. 0.3 nm/sec) , and then by Au with 200 Å (vapor

deposition rate: ca. 0.1 nm/sec). After the vapor

deposition, the glass was left to stand to lower the

temperature to 180℃ (approximately 1 hour), and the

substrate was recovered. Small-size vacuum deposition

5   apparatus VPC-260 (manufactured by ULVAC TECHNO) was

used as the vapor deposition apparatus. The thus

obtained substrate is named as F-1.

(1-2-2) Preparation of self-organized zinc porphyrin

monomolecular film (Zn-SAM F-3)

10   Compound F-3 was obtained by the reaction of the

following scheme Fa:

Scheme Fa
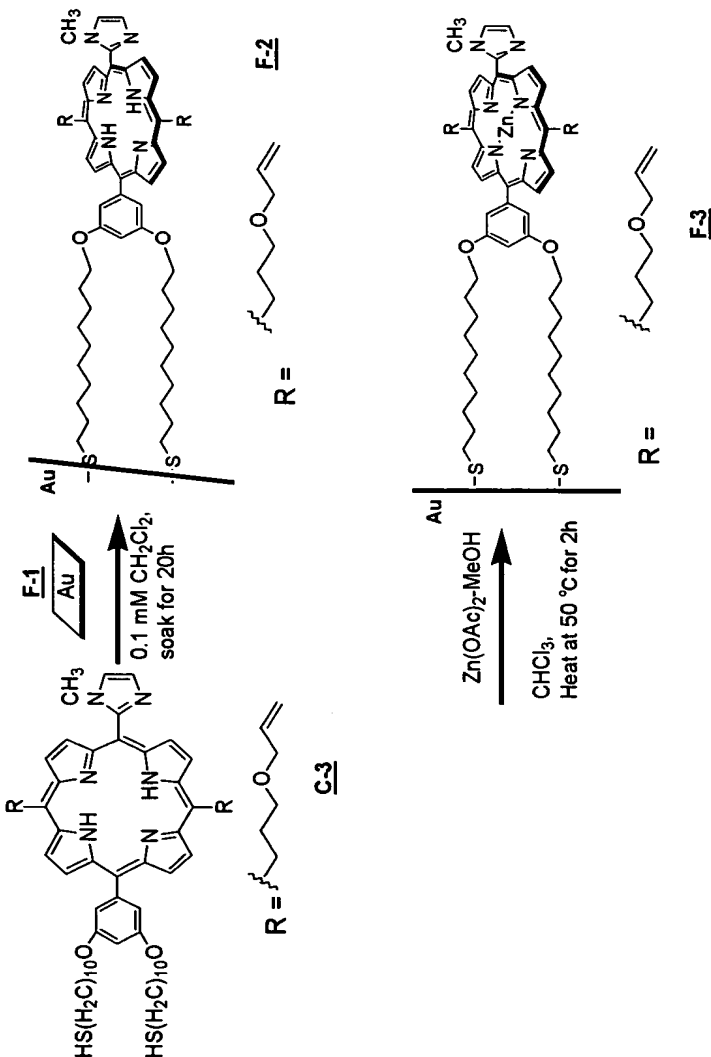
The gold substrate F-1 was divided into pieces of 10 mm $\times$ 26 mm, and the surface thereof was wiped with methanol, and then dried under nitrogen flow. 0.1 mM CH_2Cl_2 solution of C-3 was separately prepared, and argon gas was bubbled to remove air. Then the divided gold substrate was soaked into the solution overnight at room temperature. After the soaking, the surface of the substrate was washed with CH_2Cl_2. Moreover, the surface was dried with nitrogen flow, to obtain a substrate E-2 having self-organized monomolecular film. That is, the gold surface of the substrate is modified with free base porphyrin. The area occupied by porphyrin molecule on the substrate was measured by reductive elimination method of Au-S bond to reveal that the surface covering ratio was approximately 7 $\times$ 10^{13} molecule/cm^2 (10^{-10} mol/cm^2). That is, the area on the substrate occupied by 1 mol of the molecule was approximately 3 nm^2/molecule. It was confirmed that the porphyrin molecules were densely arranged all over the gold substrate.

Next, introduction of zinc to the porphyrin was effected on the substrate. Three to four drops of methanol solution of saturated zinc acetate were added to 4 mL of $CHCl_3$. After nitrogen was bubbled to remove air, Fb-SAM substrate F-2 was soaked into the solution, and heated at 50℃ for 2 hours while lightly stirring the solution with 30-minute intervals. The surface of

the substrate was washed with $CHCl_3$, MeOH and CH_2Cl_2 in this order, and dried with nitrogen flow to obtain substrate Zn-SAM F-3 having porphyrin into which zinc is introduced.

5   (1-2-3) Preparation of C60-ZnSAM/Au F-4

Compound F-4 was obtained by the reaction of the following scheme Fb:

Sceme Fb

D-3

F-4
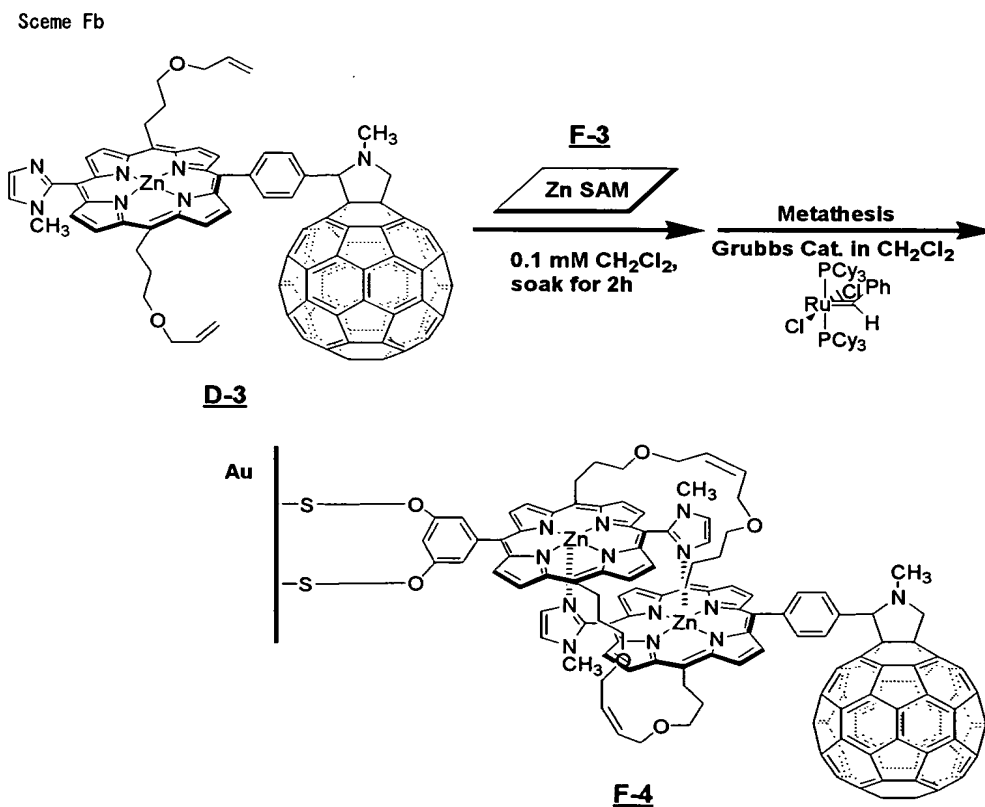
10   The substrate having porphyrinatozinc monomolecular film, Zn-SAM F-3, was soaked in 0.1 mM CH_2Cl_2 (containing 20 mM pyridene) solution of fullerene-substituted imidazolylporphyrin D-3 at room temperature for 2 hours. Then, the substrate was

15   washed with CH_2Cl_2, and dried under nitrogen flow. Further, this substrate was soaked in a solution

(Grubbs cat. 0.7 mg , 0.85 μmol in CH_2Cl_2 4 mL) of
Grubbs catalyst, benzylidene-
bis(tricyclohexyiphosphine)-dichlororuthenium
(purchased from Fluka 09587), for 10 min under nitrogen
atmosphere to effect metathesis reaction. After that,
the substrate was washed with CH_2Cl_2, MeOH and CH_2Cl_2
in this order, thereby to obtain the substrate (C60-
ZnSAM/Au) F-4, having electron acceptor attached on SAM
surface.

(1-2-4) Preparation of Antenna-ZnSAM/Au F-5

Compound F-5 was obtained by the reaction of the
following scheme Fc:

Scheme Fc

F-3

ZnSAM

1 mM CH₂Cl₂,
soak for 20h

Metathesis
Grubbs Cat in CH₂Cl₂

meso-meso-bisporphyrin E-6

F-5

The substrate F-3 was soaked (i) in 1 mM CH_2Cl_2 (containing 20 mM of pyridine) solution of meso-meso linked bisporphyrin E-6 for 1 hour, and the surface of the substrate was washed with CH_2Cl_2 in order to remove pyridine, thereby to organize oligomer of E-6 on the substrate.   This substrate was soaked in a solution of Grubbs catalyst (Grubbs cat. 0.7 mg , 0.85 μmol in CH_2Cl_2 4 mL) for 10 min under nitrogen atmosphere to effect metathesis reaction (ii).   The substrate was washed (iii) with excess CH_2Cl_2, MeOH and CH_2Cl_2 in this order to remove excess catalyst and porphyrin that is not bonded by covalent bonds, and dried under nitrogen flow.   The procedure, as one cycle, of (i) soaking, (ii) metathesis reaction, and (iii) washing were repeated for five times until the absorbance became approximately 0.15, to fix porphyrin polymer regularly.   The thus obtained substrate is named as Antenna-ZnSAM/Au F-5.

FIG. 1 shows absorption spectra of Zn-SAM F3 and the products of respective cycles.

(1-2-5)   Preparation of C60-Antenna-ZnSAM/Au F-6

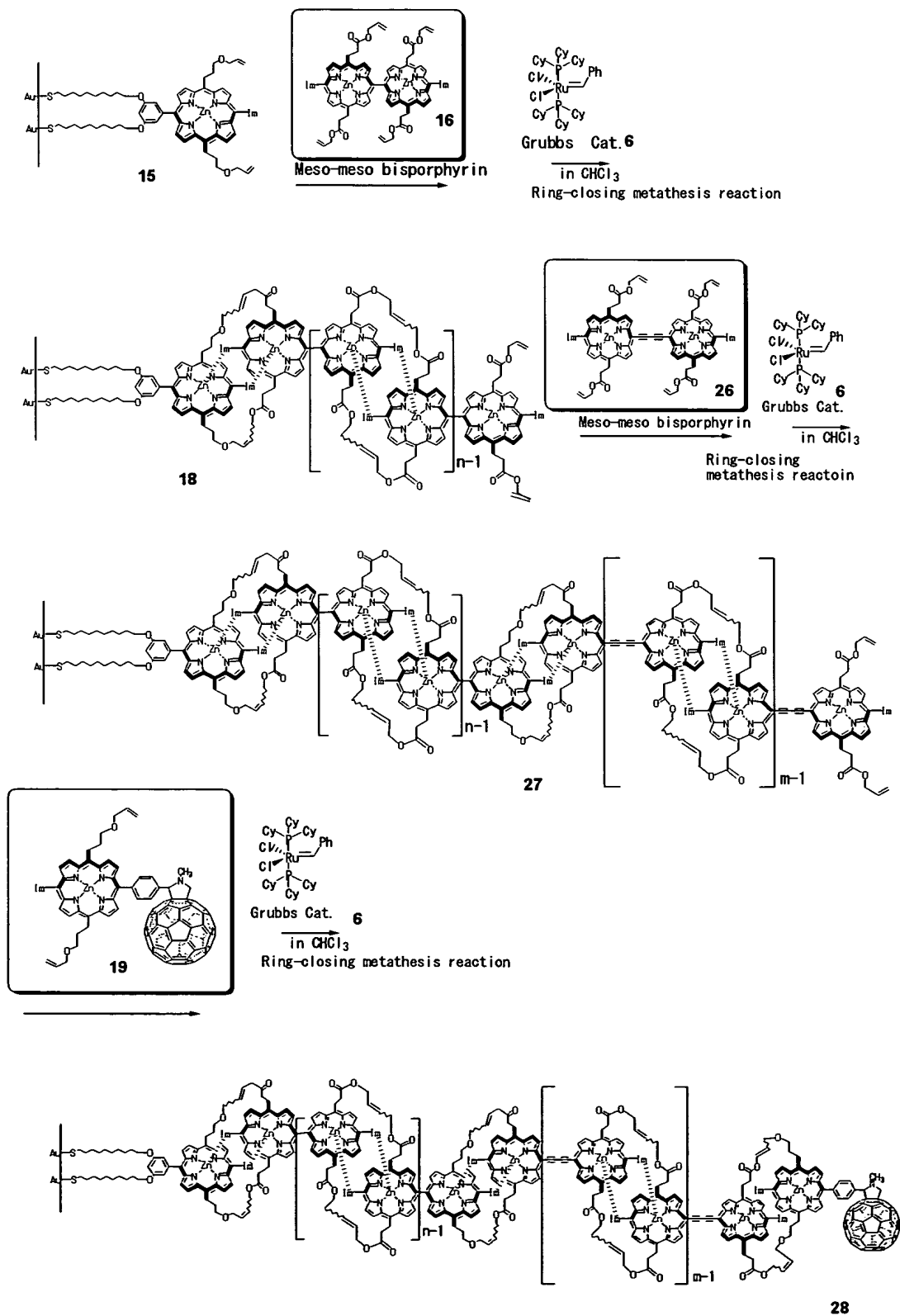Compound F-6 was obtained by the reaction of the following scheme Fd:

Scheme Fd

D-3

Metathesis
Grubbs Cat. in CH₂Cl₂

0.1 mM CH₂Cl₂
soak for 2h

F-5

F-6
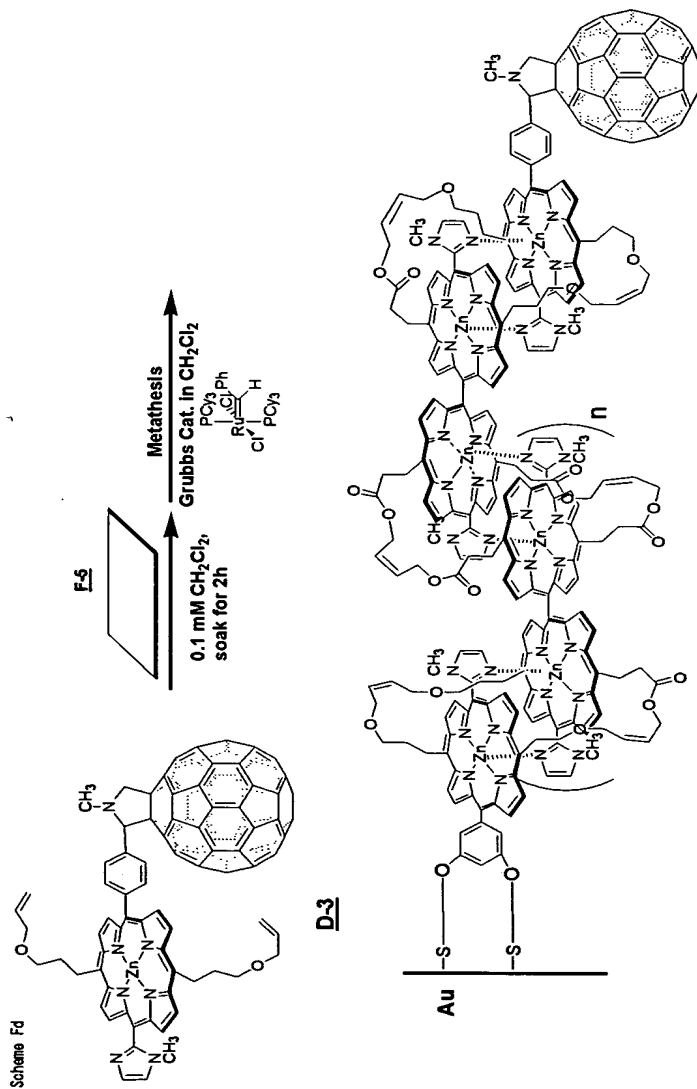
The substrate on which photo-collecting antenna is organized F-5 was soaked in 0.1 mM CH_2Cl_2 (containing 20 mM of pyridine) solution of fullerene-substituted imizazolylporphyrin D-3 for 2 hours at room temperature, then washed with CH_2Cl_2, and dried under nitrogen flow. Further, the substrate was soaked in a solution of Grubbs catalyst (Grubbs cat. 0.7 mg , 0.85 μ mol + CH_2Cl_2 4 mL) for 10 min under argon atmosphere, to effect metathesis reaction. Then, the substrate was washed with CH_2Cl_2, MeOH and CH_2Cl_2 in this order. The substrate obtained by this series of procedure is named C60-Antenna-ZnSAM/Au F-6.

<Example 2>

Although only two kinds of different porphyrin were used in Example 1 mentioned above, two or more kinds of porphyrin may be laminated and fixed in an arbitrary order. For example, as shown in scheme G below, an element having a gradient of energy level by bonding, on bis-porphyrin 16, bis-porphyrin 26 having lower energy level, and then imidazolylporphyrin having an electron acceptor, may be constructed. By such a method mentioned above, various elements each having a gradient in energy level and having hetero boundary surfaces may be constructed.

Scheme G

Meso-meso bisporphyrin **16**

Grubbs Cat.**6**

in CHCl₃
Ring-closing metathesis reaction

15

18

Meso-meso bisporphyrin **26**

Grubbs Cat. **6**

in CHCl₃

Ring-closing
metathesis reactoin

27

19

Grubbs Cat. **6**

in CHCl₃
Ring-closing metathesis reaction

28

<Example 3>

(3-1)   Measurement of photo-electronic current

Photo-electronic current of each of ZnSAM/Au F-3, C60-ZnSAM/Au F-4, Antenna-ZnSAM/Au F-5 and C60-Antenna-ZnSAM/Au F-6 prepared in Example 1 was measured.

(3-2)   Apparatus for the measurement

200 W Hg-Xe lamp

Electronic power supply: XENON LAMP POWER SUPPLY C7535 HAMAMATSU

Lamp housing: LAMPHOUSE UNIT E7536 HAMAMATSU

Monochrome meter: SPG-120S SHIMADZU

(3-3)   Measurement system

The photo-electrochemistry cell (FIG. 2) in which optical cell is combined with tri-pole electrochemical triode electrochemical cell was used.   The gold electrode (working electrode) on which porphyrin is modified was fixed in the cell via rubber having a window of 0.28 cm^2.   The cell was set at a position of 30 cm away from the housing of 200-W Xe lamp.   White light or monochrome light was irradiated to the surface of the substrate through optical cell using IR cut filter or monochrome meter.   In order to remove the influence of the light from out side, the whole apparatus was covered with a box to shield light.

The cell was filled with 0.1 M Na_2SO_4 aqueous solution, as a supporting electrolyte, and 5 mM methylviologen aqueous solution for sacrificial agent.

Photo-electronic current was measured after the counter electrode (platinum wire) and the reference electrode (Ag/Ag+, CH_3CN, tetra-t-butylammonium perchlorate (TBAP)) were soaked in the solution and nitrogen was bubbled therethrough for 1 hour.

After the initiation of the measurement, the current was stabilized by letting the shutter off for 50 min. Then, light irradiation was changed between on and off in an interval of 20 sec.

The relationship between electric current and voltage at the times of light irradiation and non-irradiation of the prepared substrates ZnSAM/Au F-3, C60- ZnSAM/Au F-4, Antenna-ZnSAM/Au F-5 and C60-Antenna-ZnSAM/Au F-6 were measured using the above apparatus. The results are shown in FIGS. 3 and 4.

The relationship between electric current and voltage at the times of light irradiation and non-irradiation of Antenna-ZnSAM/Au F-5 was also measured by changing the electrolyte to 50 mM triethanolamine. The results are shown in FIG. 5.

The element represented by the formula (VIII) or (VIII') having a polymer on a substrate is able to be used as photo-functional element by the function of photo-excited electron transfer of porphyrin, which is a constituting unit. Specifically, the photo-functional element of the present invention is expected to be applied to organic solar cell and third-order

non-linear organic material.

Also, in the photo-functional element of the present invention, the porphyrin polymer that is organized by coordination bonds on a substrate is fixed by covalent bonds. Especially, the fixation by the covalent bonds renders the photo-functional element of the present invention to less dependent on the circumstance (a solvent to be used) in which the photo-functional element of the present invention is used. As a result, the configuration of the polymer is maintained stably. In addition, the possibility of detaching the already laminated layer during the soaking step for laminating the polymer and a washing step of the laminate. As a result, a laminate having a large thickness may be formed.

Also, in the photo-functional element of the present invention, porphyrin to be fixed may be arbitrarily selected, and the element may be grown step by step toward one direction only. Accordingly, for example, when porphyrin polymers having different energy levels are fixed step by step, a functional material having a gradient of electric level may be obtained. Due to this, the direction of electrons holes may be control (rectification).

Also, the photo-functional element of the present invention has advantages, in comparison with conventional electric materials using inorganic

semiconductor, such as a possibility of weight decrease (weight saving), a possibility of thin layer formation, resistance to bending, lower cost, and decomposition by nature after the use thereof.

5   Additional advantages and modifications will readily occur to those skilled in the art. Therefore, the invention in its broader aspects is not limited to the specific details and representative embodiments shown and described herein. Accordingly, various

10   modifications may be made without departing from the spirit or scope of the general inventive concept as defined by the appended claims and their equivalents.